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HOMOLYTIC SUBSTITUTION IN INDOLINONE NITROXIDES - IV.[1] REACTIONS WITH AMINYL RADICALS. A SPECTROSCOPIC AND CRYSTALLOGRAPHIC STUDY.

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Abstract: The reactions between 2,2-diphenyl-indolinone-N-oxyl **(3)** and a series of aminyl radicals generated in situ by oxidation of secondary aromatic amines with PbO_2 lead to aminated hydroxylamines **(4)**, which in the presence of PbO_2 are converted to the aminated nitroxides **(5)**. When starting from primary amines, these are further oxidated to quinonimine-N-oxides **(6)** which then undergo nucleophilic substitution by another amine molecule to give the diaminated hydroxylamines **(7)**. These are further oxidated to nitroxides **(8)**, the final products of the reaction being the aminated quinone-diimine-N-oxides **(9)**. The paramagnetic species **(5)** and **(8)** have been characterized using ESR spectroscopy; in addition, the molecular geometry of one of the N-oxides **(9)** was elucidated by means of X-ray structure analysis.

Indolinone-N-oxyls, likewise other nitroxides,[2] exhibit a remarkable reactivity towards nucleophilic radicals via coupling at the nitroxide function: for example 2,2-diphenylindolinone-N-oxyl **(3)** reacts quantitatively with methyl radicals to give the corresponding methylhydroxylamine.[1] On the other hand the reaction of indolinone-N-oxyls with electrophilic radicals leads to ring substitution in positions 5 and 7: thus the reaction of **(3)** with benzoyl peroxide yielded 5- and 7-monobenzoyloxy derivatives together with some 5,7-disubstituted compound.[3] A similar reactivity pattern was established for the reaction with tert-butoxyl radicals[1] (mono- and di-tert-butoxy derivatives) and with peracids (mono- and di-aroyloxy derivatives),[4] although in the light of recent results serious doubts may be cast as to the homolytic nature of the last reaction.[5]

One might anticipate that aminyl radicals, due to their well established electrophilic character, would give similar substitution reactions. Nevertheless, there are no available examples of direct amination by means of aminyl radicals:[6] indeed aminyls from primary and secondary aromatic amines dimerize affording hydrazino- and azo-compounds,[7] respectively, while aminyls from aliphatic amines mainly lead to combination and disproportionation products.[8] Aryl-alkyl aminyls are also known to give hydrogen abstraction reactions,[9] although aminyls are classified as weak dehydrogenating agents, able to abstract only activated hydrogens.[10] The hydrogen abstracting ability of aminyls is however enhanced by the introduction of such substituents which are able to inhibit the occurrence of self reactions.

We report here that direct amination of indolinone-N-oxyl is brought about by aminyl radicals from aromatic amines to give products that may or may not undergo further reactions depending on the nature of the starting amine. With aminyl radicals from secondary aromatic amines the reaction product are the 5-substituted hydroxylamines, while when starting from primary aromatic amines quinone-diimine-N-oxides are obtained; these then undergo a nucleophilic attack by a molecule of amine leading to 4-arylamino-substituted quinone-diimine-N-oxides.

RESULTS AND DISCUSSION

Product studies and ESR studies - The reaction between indolinone-N-oxyl **(3)** and amines in the presence of lead dioxide led to different products depending on the nature of the amine (i.e., primary or secondary amines) as outlined in **Scheme I.** In a typical experiment, **3** was reacted at room temperature with a primary or secondary amine in the presence of an excess of PbO_2 (1:2:4 molar ratio, respectively), until the color of the reaction mixture changed from the original red to a deep green (secondary amines) or purple (primary amines). In the presence of PbO_2 the amines **(1)** are oxidized to aminyl radicals **(2)**[11,12] that react with the indolinonic nitroxide **(3)** to give the hydroxylamines **(4)**, which in the reaction medium are oxidized to nitroxides **(5)**. These are the final reaction products in the case of aminyls from secondary amines, as they cannot undergo further oxidation. On the contrary, when R = H, nitroxides **(5)** are converted, under the reaction conditions, to the quinone-diimines **(6)**, which in turn are subject to a nucleophilic attack by the starting primary amines **(1)** to give the disubstituted hydroxylamines **(7)**. These, in the presence of the excess lead dioxide, are converted to the nitroxide **(8)** and eventually to the substituted quinone-diimines **(9)**. The isolated products were nitroxides **(5a)** and **(5b)**, when starting from secondary amines, and quinone-diimines **(6c-f)** and **(9c-e)**, when starting from primary amines. The yields and spectroscopic data are collected in Tables 1 and 2, respectively. Nitroxides **(5a)** and **(5b)** were fairly persistent radicals which could be isolated and crystallized. They could therefore be characterized by means of ESR spectroscopy: the measured hyperfine coupling constants (Table 3) are consistent with those previously reported for other related species. The ESR spectrum of **3** shows a nitrogen splitting of ca. 9.3 Gauss, a 1:2:1 triplet with a separation of ca. 3.2 Gauss attributed to the hydrogen atoms in positions 5 and 7, and a second 1:2:1 triplet with a smaller separation (ca. 1.0 Gauss) originating from hydrogens in positions 4 and 6.[13] The introduction of a substituent in position 5 changes the larger triplet splitting to a 1:1 doublet with a separation of ca. 2.7 Gauss; similarly, substitution in position 7 leads again to a 1:1 doublet, which however is characterized by a somewhat larger coupling constant (ca. 3.2 Gauss).[1] Although apparently small (0.5 Gauss), these differences are always observed with a variety of substituents[1,3,14] and therefore the value of the doublet splitting in monosubstituted indolinone-N-oxyls provides an useful tool to determine which of the two positions 5 and 7 has been substituted.

Table 1 - Yields (mmoles) of compounds **(5)**, **(6)** and **(9)** in the reaction of nitroxide (**3**, 1 mmole) with aromatic amines (**1a-f**, 2 mmoles).*

Amine	**Product**	**Yield**
1a	**5a**	0.31
1b	**5b**	0.53
1c	**6c**	0.29
	9c	0.36
1d	**6d**	0.1
	9d	0.53
1e	**6e**	0.1
	9e	0.38
1f	**6f**	0.28

*) Variable amounts of **(3)** were also recovered in each reaction.

Table 2 - Physical and spectroscopic properties of compounds (**6c**, **6e**, **f** and **9c–e**).[a]

Comp	m.p.[b]	I.R. (νmax)[c]	^{1}H NMR (δ)[d]
5a[e]	---	1717^{f}-1595^{g}	
5b	130	1720^{f}-1590^{g}	
6c	194	1745^{f}-1592^{h}	3.77(s,3H,OMe) 6.8(s5H,Ar) 7.04-7.44(m,12H,Ar)
6e	---	1747^{f}-1610^{g} 1585^{d}	6.93(d,1H,Ar:J=0.4Hz) 7.1-7.7(m,17H,Ar)
6f	105	1747^{f}-1605^{g} 1585^{h}	6.83-7.73(m,Ar)
9c	176	3200^{i}-1695^{f} 1605^{g}-1585^{h}	3.73(s,3H,OMe) 3.77(s,3H,OMe) 6.69(A_2B_2,4H,Ar) 6.81(s,5H,Ar) 7.18(A_2B_2,4H,Ar) 7.18(s,10H,Ar) 8.69(br,1H,NH)
9d	130	3250^{i}-1715^{f} 1590^{h}	2.34(s,3H,Me) 2.40(s,3H,Me) 6.78-7.56(m,20H,Ar) 8.88(br,1H,NH)
9e	198	3210^{i}-1710^{f} 1610^{g}-1585^{h}	6.76-7.76(m,22H,Ar) 8.83(br,1H,NH)

a, all compounds showed proper molecular ion peaks in the mass spectra; b, in centigrades, products crystallized from benzene/petroleum ether; c, in nujol (cm^{-1}); d, in $CDCl_3$; e, uncrystallizable; f, C=O; g, PhNH-C-; h, C=N; i, NH.

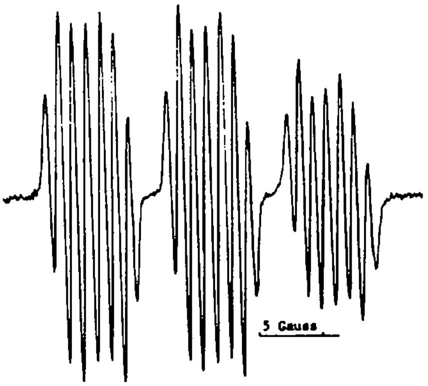
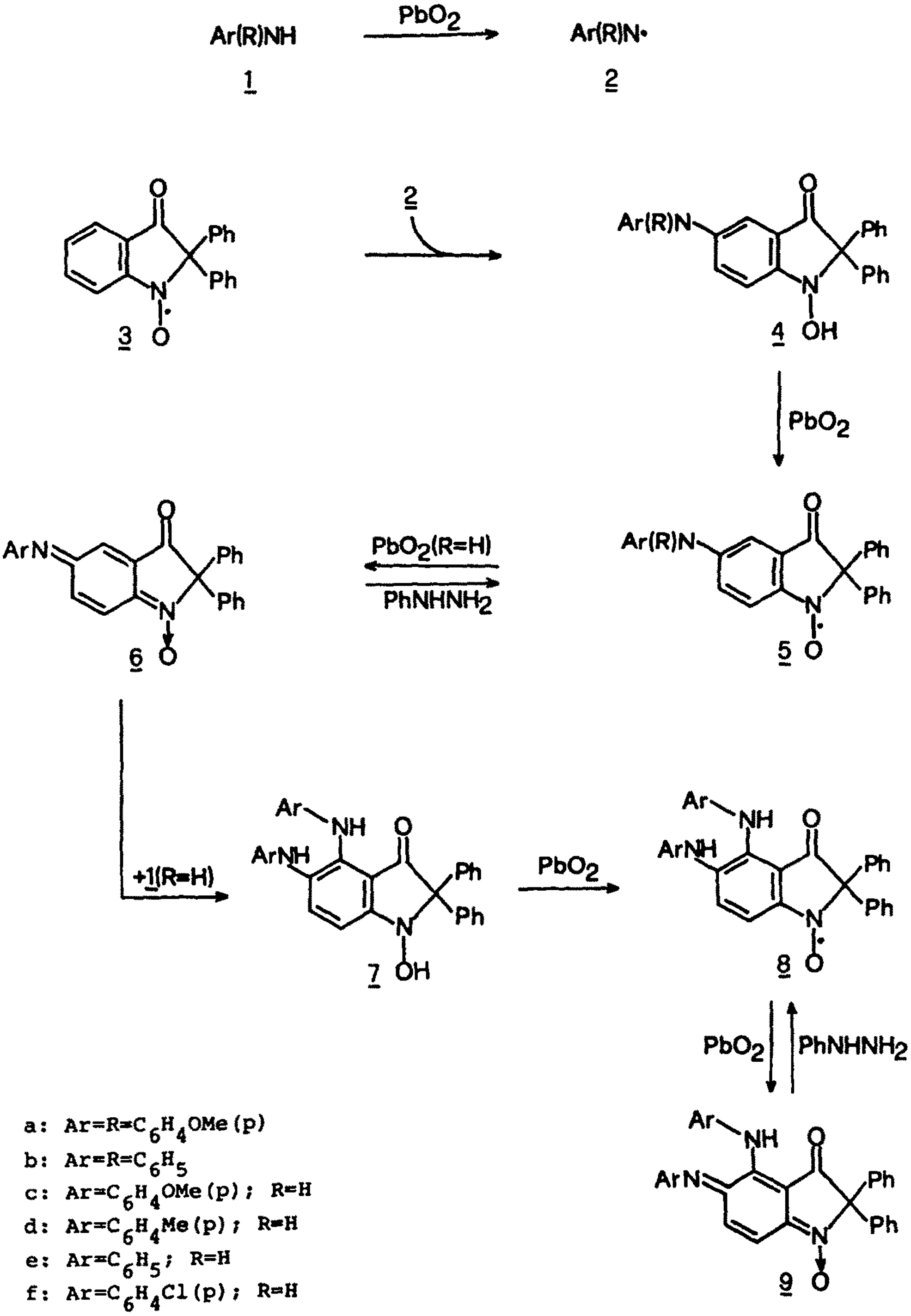


Figure 1 - Room temperature ESR spectrum of radical **8c**.

It follows that the values of the doublet splitting measured for **5a** (2.82 Gauss) and **5b** (2.84 Gauss), together with the further nitrogen splitting a_N of about 0.95 Gauss, are a clear indication of the introduction of a NR_2 substituent in position 5 of nitroxide (**3**). This identification of compounds **5a** and **5b** received additional support from their IR spectra, which exhibited absorptions at ca. 1720 cm^{-1} (carbonyl group) and 1590 cm^{-1}, this latter absorption being typical of the indolinic system,[15] and from their mass spectra which showed the correct molecular ion peaks.

In the case of aminyls from primary amines, the isolated products were **6c–f** and **9c–e**. Actually, nitroxides (**5c–f**) cannot be isolated directly from the reaction mixture because, as soon as formed, they undergo oxidation by the excess PbO_2 to the corresponding quinone-diimines (**6**), ESR experiments indicated however that isolated **6c–f** were contaminated by small amounts of the related nitroxides. The signals due to these impurities, which were in all cases consistent with a 5-substituted indolinonic-N-oxyl, could be wiped off by adding some PbO_2 to the solution of the quinone-diimine or, conversely, could be enhanced by addition of a reducing agent, such as phenylhydrazine. The structure of compounds (**6**) was also established by ^{1}H NMR and mass spectroscopy



a: Ar=R=$C_6H_4OMe(p)$

b: Ar=R=C_6H_5

c: Ar=$C_6H_4OMe(p)$; R=H

d: Ar=$C_6H_4Me(p)$; R=H

e: Ar=C_6H_5; R=H

f: Ar=$C_6H_4Cl(p)$; R=H

Scheme I

Table 3 - ESR hfs constants (Gauss) of radicals **5a-f**, **8c-e**, **10d** and **10f**.

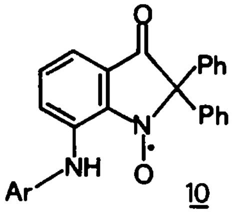
Radical	Solv.	$a(N_1)$	$a(H_4)$	$a(H_6)$	$a(H_7)$	$a(N_5)$	g	
5a	C_6h_6	9.31	1.01	1.01	2.72	0.88	2.0056	
	$CHCl_3$	9.67	0.88	0.88	2.82	1.20	2.0055	
5b	$CHCl_3$	9.56	0.98	0.98	2.84	0.86	2.0055	
5c	C_6H_6	9.57	1.04	1.04	2.66	0.90	2.0054	
5d	C_6H_6	9.50	1.00	1.00	2.76	0.94	2.0055	
	$CHCl_3$	9.87	0.95	0.95	2.85	0.91	2.0054	
5e	C_6H_6	9.47	0.90	0.90	2.75	0.84	2.0056	
	$CHCl_3$	9.78	0.92	0.92	2.76	0.92	2.0055	
5f	C_6H_6	9.44	0.96	0.96	2.78	0.78	2.0056	
	$CHCl_3$	9.76	0.96	0.96	2.76	0.86	2.0055	
8c	C_6H_6	9.36		1.04	3.18	1.00	2.0055	
	$CHCl_3$	9.74		1.18	3.36	1.14	2.0053	
8d	C_6H_6	9.35		1.10	3.20	0.86	2.0058	
	$CHCl_3$	9.72		1.14	3.38	1.04	2.0054	
8e	C_6H_6	9.26		1.24	3.09	0.62	2.0052	
	$CHCl_3$	9.62		1.12	3.26	0.88	2.0054	
		$a(N_1)$	$a(H_4)$	$a(H_5)$	$a(H_6)$	$a(N_7)$	$a(H_{NH})$	g
10d	$CHCl_3$	9.93		3.14	1.36	1.32	0.40	2.0053
10f	C_6H_6	9.90	1.10	3.13	1.10	0.78	0.70	2.0054

(Table 2), and it appears worthwhile pointing out here that none of compounds **(6c-f)** showed in its IR spectrum the absorption in the region around 1590 cm^{-1}, typical of the indolinic structure.

Compounds **(9)**, which were isolated from the reactions of all primary amines with the exception of p-chloroaniline, were characterized by NMR and mass spectrometry. Upon reduction with less than one equivalent of $PhNHNH_2$, these substituted quinone-diimines afforded nitroxides **(8)**, whose ESR spectra exhibited, beside the coupling with the nitrogen of the nitroxidic function, couplings with a nitrogen atom (presumably the one in position 5) and with the two hydrogen atoms in positions 6 and 7, the splittings from this last nucleus being somewhat larger than those observed in nitroxides **(5)**. Although the slight increase of spin density at position 7 in radicals **(8)** may be expected because of a conjugative interaction with the amino substituent in position 4, an identification of compounds **(9)** based exclusively on the ESR spectral parameters of the corresponding nitroxides might appear questionable. However at least in one case, i.e. in the case of **9c**, an unambiguous elucidation of the structure was achieved by means of X-ray diffractometric studies (see below).

In order to verify the reaction sequence proposed in the second part of **Scheme** I from compounds **(6)** onward, a solution of pure **6c** was reacted with p-anisidine. The substituted quinone-diimine **(9c)** was again isolated, and its formation is believed to proceed via nucleophilic addition of the amine to the quinonoid system[16,17] followed by in situ oxidation by atmosferic oxygen of the first formed hydroxilamine **(7c)**. The nucleophilic nature of the step from **6** to **7** is further substantiated by the fact that of all the primary amines used in the reaction with compound **(3)**, only p-chloroaniline failed to give the substituted quinone-diimine **(9f)**, what can be readily understood if considering the low nucleophilic character of this amine.

As to the positional selectivity of the nucleophilic substitution, it is interesting to note that the attack of the second amine occurs specifically at position 4 and that no traces of the 6-substituted isomer are detected. This positional preference may be viewed as the result of the combined conjugative effects exerted on position 4 by both the carbonyl an the N-oxide functions of the quinone-diimine **(6)**.



10

d: Ar=$C_6H_4Me(p)$
f: Ar=$C_6H_4Cl(p)$

In the reactions of indolinone **(3)** with p-toluidine and with p-chloroaniline, traces of two additional compounds were detected. Due to their small amounts they could not be fully analized, but their mass spectra showed the molecular ion peaks corresponding to monosubstituted indolinone-N-oxyls; however their ESR spectra differed from those of radicals **5d** and **5f** in that they showed a larger doublet splitting, i.e. 3.14 and 3.13 Gauss, respectively. In the light of what previously said about the ESR spectral parameters of the unsubstituted and 5-monosubstituted indolinone-N-oxyls **3** and **5**, we identify these two paramagnetic compounds as the 7-(p-tolylamino)indolinone-N-oxyl **(10d)** and 7-(p-chlorophenylamino)indolinone-N-oxyl **(10f)**.

Molecular geometry - Structural studies were carried out only for 2,2-diphenyl-4-(p-methoxyphenylamino)-5-(p-methoxyphenylimino)indolin-3-one-N-oxide **(9c)** because of the difficulty of growing crystals suitable for X-ray diffractometric studies in the case of other compounds of general structure **6** or **9**. Figure 2 shows a drawing of the molecule where the arbitrary crystallographic numbering scheme is indicated; Table 4 lists bond distances and angles.[*][°] The conformational geometry of the molecule was deduced from the torsion angles (Table 4) and from the analysis of the planarity reported in Table 5.

Bond distances and angles in **9c** are mostly as expected from hybridization of the atoms. The configuration of the N-oxide group is in a reasonable agreement with that found for the unsubstituted radical **(3)**,[18] the oxygen atom O(1) being 0.080(3)Å out of the C(1)-N(1)-C(8) plane; yet, the N(1)-O(1) bond is significantly longer (1.295(3)Å) than the corresponding bond in **3** (1.250(6)Å).[18]

An examination of the values of the carbonyl O(2)-C(2) (1.218(3)Å), C(2)-C(3) (1.454(3)Å), C(3)-C(4) (1.384(2)Å), C(4)-C(5) (1.494(3)Å) and imino C(5)-N(3) (1.293(2)Å) bond lengths indicates a conjugative interaction between the p orbital of the iminic nitrogen N(3) and that of the carbonylic O(2); on the other hand, the values of C(5)-N(3) (1.293(2) Å), C(5)-C(6) (1.454(3) Å), C(6)-C(7) (1.341(2) Å), C(7)-C(8) (1.418(3) Å) and C(8)-N(1) (1.321(2) Å) also indicate significant conjugation between N(3) and the heterocyclic nitrogen N(1). This suggests that the six-membered ring of the indolinonic system should be assigned a rigid quinonone-like structure.

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[*] The atomic co-ordinates are available from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[°] Supplementary data available: Atomic fractional co-ordinates; Puckering and asymmetry parameters, and list of thermal parameters and structure factors.

Table 4 - Bond distances (Å), bond angles(°), and selected torsion angles(°) with esd's in parenthesis.

a) Bond distances

O(1)-N(1)	1.295(3)	C(2)-C(3)	1.454(3)	C(22)-C(23)	1.383(3)
O(2)-C(2)	1.218(3)	C(3)-C(4)	1.384(2)	C(23)-C(24)	1.383(3)
O(21)-C(24)	1.369(3)	C(3)-C(8)	1.437(3)	C(24)-C(25)	1.376(4)
O(21)-C(27)	1.424(6)	C(4)-C(5)	1.494(3)	C(25)-C(26)	1.388(3)
O(31)-C(34)	1.381(3)	C(5)-C(6)	1.454(3)	C(31)-C(32)	1.378(3)
O(31)-C(37)	1.412(4)	C(6)-C(7)	1.341(2)	C(31)-C(36)	1.395(3)
N(1)-C(1)	1.503(3)	C(7)-C(8)	1.418(3)	C(32)-C(33)	1.395(4)
N(1)-C(8)	1.321(2)	C(11)-C(12)	1.383(3)	C(33)-C(34)	1.376(4)
N(2)-C(4)	1.348(3)	C(11)-C(16)	1.391(3)	C(34)-C(35)	1.376(3)
N(2)-C(21)	1.420(3)	C(12)-C(13)	1.396(4)	C(35)-C(36)	1.377(4)
N(3)-C(5)	1.293(2)	C(13)-C(14)	1.365(4)	C(91)-C(92)	1.376(3)
N(3)-C(31)	1.419(3)	C(14)-C(15)	1.362(3)	C(91)-C(96)	1.384(3)
C(1)-C(2)	1.566(3)	C(15)-C(16)	1.386(4)	C(92)-C(93)	1.389(4)
C(1)-C(11)	1.527(3)	C(21)-C(22)	1.388(3)	C(93)-C(94)	1.370(3)
C(1)-C(91)	1.526(2)	C(21)-C(26)	1.378(3)	C(94)-C(95)	1.371(4)
				C(95)-C(96)	1.389(3)

b) Bond angles

C(24)-O(21)-C(27)	117.3(3)	C(11)-C(12)-C(13)	120.7(3)
C(34)-O(31)-C(37)	117.7(3)	C(12)-C(13)-C(14)	120.5(4)
O(1)-N(1)-C(1)	121.2(2)	C(13)-C(14)-C(15)	119.4(4)
O(1)-N(1)-C(8)	126.4(3)	C(14)-C(15)-C(16)	121.2(3)
C(1)-N(1)-C(8)	112.3(2)	C(11)-C(16)-C(15)	120.4(3)
C(4)-N(2)-C(21)	128.9(2)	N(2)-C(21)-C(22)	121.8(3)
C(5)-N(3)-C(31)	121.0(3)	N(2)-C(21)-C(26)	118.8(2)
N(1)-C(1)-C(2)	101.0(2)	C(22)-C(21)-C(26)	118.9(3)
N(1)-C(1)-C(11)	110.4(2)	C(21)-C(22)-C(23)	120.3(3)
N(1)-C(1)-C(91)	107.5(3)	C(22)-C(23)-C(24)	120.3(3)
C(2)-C(1)-C(11)	112.3(2)	O(21)-C(24)-C(23)	115.5(2)
C(2)-C(1)-C(91)	111.4(1)	O(21)-C(24)-C(25)	124.9(3)
C(11)-C(1)-C(91)	113.4(2)	C(23)-C(24)-C(25)	119.7(4)
O(2)-C(2)-C(1)	122.9(2)	C(24)-C(25)-C(26)	119.9(3)
O(2)-C(2)-C(3)	129.6(2)	C(21)-C(26)-C(25)	120.9(2)
C(1)-C(2)-C(3)	107.4(2)	N(3)-C(31)-C(32)	124.3(2)
C(2)-C(3)-C(4)	133.5(3)	N(3)-C(31)-C(36)	116.8(4)
C(2)-C(3)-C(8)	106.9(2)	C(32)-C(31)-C(36)	118.8(4)
C(4)-C(3)-C(8)	119.3(2)	C(31)-C(32)-C(33)	120.4(3)
N(2)-C(4)-C(3)	127.9(4)	C(32)-C(33)-C(34)	119.6(4)
N(2)-C(4)-C(5)	114.4(2)	O(31)-C(34)-C(33)	123.8(4)
C(3)-C(4)-C(5)	117.7(3)	O(31)-C(34)-C(35)	115.5(2)
N(3)-C(5)-C(4)	115.4(3)	C(33)-C(34)-C(35)	120.7(3)
N(3)-C(5)-C(6)	126.6(3)	C(34)-C(35)-C(36)	119.6(3)
C(4)-C(5)-C(6)	117.8(2)	C(31)-C(36)-C(35)	120.8(3)
C(5)-C(6)-C(7)	122.8(4)	C(1)-C(91)-C(92)	121.0(3)
C(6)-C(7)-C(8)	118.0(2)	C(1)-C(91)-C(96)	120.5(2)
N(1)-C(8)-C(3)	112.1(2)	C(92)-C(91)-C(96)	118.5(2)
N(1)-C(8)-C(7)	124.9(2)	C(91)-C(92)-C(93)	120.7(4)
C(3)-C(8)-C(7)	123.0(2)	C(92)-C(93)-C(94)	120.3(3)
C(1)-C(11)-C(12)	122.4(2)	C(93)-C(94)-C(95)	119.7(3)
C(1)-C(11)-C(16)	119.6(3)	C(94)-C(95)-C(96)	120.1(4)
C(12)-C(11)-C(16)	118.0(3)	C(91)-C(96)-C(95)	120.7(3)

c) Selected torsion angles.

C(27)-O(21)-C(24)-C(25)	-6.3(6)	C(31)-N(3)-C(5)-C(6)	-5.4(6)
C(37)-O(31)-C(34)-C(33)	1.1(6)	N(1)-C(1)-C(2)-O(2)	-173.4(4)
O(1)-N(1)-C(8)-C(3)	179.7(4)	C(11)-C(1)-C(2)-O(2)	69.0(5)
O(1)-N(1)-C(8)-C(7)	-0.8(6)	C(91)-C(1)-C(2)-O(2)	-59.5(5)
O(1)-N(1)-C(1)-C(2)	176.8(3)	O(2)-C(2)-C(3)-C(4)	-3.6(7)
O(1)-N(1)-C(1)-C(11)	-64.3(5)	O(2)-C(2)-C(3)-C(8)	170.4(4)
O(1)-N(1)-C(1)-C(91)	60.0(4)	C(2)-C(3)-C(4)-N(2)	-17.8(7)
C(4)-N(2)-C(21)-C(22)	-31.2(6)	C(8)-C(3)-C(4)-N(2)	168.7(4)
C(21)-N(2)-C(4)-C(3)	-29.2(7)	N(2)-C(4)-C(5)-N(3)	8.6(5)
C(21)-N(2)-C(4)-C(5)	150.8(4)	C(3)-C(4)-C(5)-N(3)	-171.4(4)
C(5)-N(3)-C(31)-C(32)	-54.0(6)	N(2)-C(4)-C(5)-C(6)	-166.8(3)
C(31)-N(3)-C(5)-C(4)	179.7(3)	N(3)-C(5)-C(6)-C(7)	179.2(4)

d) Bond distances involving hydrogen atoms are in the range 0.86(3) to 1.17(7) Å.

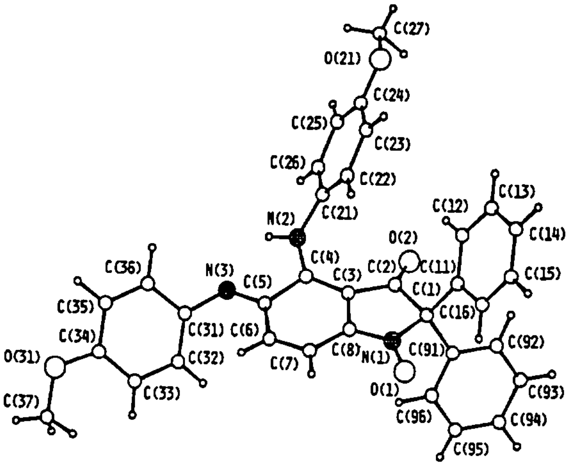

Figure 2 - Drawing of the molecule of compound **9c**, showing the arbitrary crystallographic numbering scheme.

The puckering co-ordinates[19] indicate that this ring adopts a conformation in between a boat and a twist-boat, while the asymmetry parameters[20] do not suggest the presence of particular symmetry.

The five-membered ring appears to be in a situation intermediate between a twist and an envelope conformation, with the amplitude-phase puckering co-ordinates[19] Q = 0.057(3) Å and φ = 112(3)°. A quantitative evaluation of this deformation can be derived from the asymmetry parameters proposed by Duax et al.[20] which indicate that a reasonable symmetry is induced by the presence of a pseudo-mirror plane through C(3) and of a two-fold rotational axis through C(1). The dihedral angle between the mean plane containing the six-membered ring and five-membered ring of the indolinonic unit is 7.5(1)°.

The orientation of the two phenyl rings at C(1) is mainly determined by steric interactions and the dihedral angles formed with the mean plane of the five-membered rings are 121.9(1)° and 73.5(1)° for the rings containing C(11) and C(91), respectively. Steric effects are also held responsible for the significant deviation from planarity exhibited by the benzene rings bearing the methoxy substituents, the deviation being more noticeable for the ring containing the C(31) carbon atom. The reciprocal orientation of the planar parts of the molecule can be defined in terms of the dihedral angles reported in Table 5.

The short contact N(2)...N(3) 2.613(3), H(2)...N(3) 2.10(2)Å; N(2)-H(2)...N(3) 117(3)° suggests the presence of an intramolecular hydrogen bond between the imino and amino nitrogen atoms.

Molecular packing is determined by a long intermolecular hydrogen bond of the type N-H...O bridging the amino-nitrogen N(2) and the carbonyl oxygen O(2) in -x +1/2, y-1/2, -z -1/2 position: N(2)...O(2) 3.136(2), H(2)...O(2) 2.49(3)Å; N(2)-H(2)...O(2) 133(2)°.

Other contacts are consistent with Van der Waals interactions.

EXPERIMENTAL

Nitroxide **(3)**[13] and fresh lead dioxide[21] were prepared according to literature methods, while all starting amines, with the exception of **1a** were commercially available (Carlo Erba).

^{1}H NMR spectra were recorded on a Varian 90 MHz spectrometer using TMS as internal standard; IR spectra were recorded using a Perkin-Elmer 257 spectrophotometer, while mass spectra were obtained with a Varian MAT 112 S spectrometer.

a) Reactions of nitroxide (3) with aromatic amines (1a-f). PbO_2 (960 mg, 4 mmole) was added to the solution of nitroxide **(3)** (300 mg, 1 mmole) and **1a** (226 mg, 2 mmole) in 30 ml of CH_2Cl_2 under stirring at room temperature. The red colour of the starting solution turned to green with time. After 1 h an additional mmole of PbO_2 was added to the solution. After 4-5 hours the solution was filtered, and the filtrate concentrated to dryness. With amines **(1c-f)** the colour turned to purple at the end of the reaction. The residue was dissolved in benzene and chromatographed through a silica gel column. A similar procedure was used with all other amines.

In the case of the secondary amines **1a** and **1b** compounds **(5a)** and **(5b)** were isolated from the

Table 5 - Analysis of the planarity.

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a) Distances (in 10^3 Å) of relevant atoms from the mean plane with standard deviations in parentheses: starred atoms were not used to define the plane.

Plane A: N(1), C(1), C(2), C(3), C(8)
N(1) -14(3), C(1) -9(3), C(2) 27(3), C(3) -36(3), C(8) 32(3), O(1)* 22(3), O(2)* 158(3)
Plane B: C(3)-C(8)
C(3) 27(3), C(4) -81(3), C(5) 59(3), C(6) 4(3), C(7) -49(3), C(8) 20(3), N(1)* 95(3), N(2)* -301(3), N(3)* 125(3), C(2)* 276(3)
Plane C: C(11)-C(16)
C(11) -3(3), C(12) 6(4), C(13) -3(4), C(14) -2(4), C(15) 4(4), C(16) -1(3)
Plane D: C(21)-C(26)
C(21) 7(2), C(22) -5(2), C(23) -2(3), C(24) 6(2), C(25) -6(3), C(26) -2(2), O(21)* 34(2), N(2)* 198(2)
Plane E: C(31)-C(36)
C(31) -19(2), C(32) 10(3), C(33) 20(4), C(34) -9(2), C(35) -13(4), C(36) 20(2), O(31)* -26(2), N(3)* -15(2)
Plane F: C(91)-C(96)
C(91) -3(3), C(92) 2(4), C(93) 2(4), C(94) -3(4), C(95) 0(4), C(96) 2(3)
Plane G: C(24), O(21), C(27)
Plane H: C(34), O(31), C(37)

b) Angles between planes (°)

AB	7.5(1)	BD	53.4(1)	DE	94.9(1)
AC	121.9(1)	BE	52.6(1)	DG	6.2(3)
AF	73.5(1)	CF	102.9(1)	EH	0.7(2)

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first eluted blue fraction (see Tables 1-3 for yields and spectroscopic data), while from the second, red, fraction the starting nitroxide was recovered in 62% and 38% yields respectively. With primary aromatic amines **(1c-f)**, after elution with acetone/benzene 5/95, **6** and **9** were isolated from the red and blue fraction, respectively; in some cases **6** and **9** were further purified on a preparative silica gel tlc (ethyl acetate/cyclohexane 2/8). The starting nitroxide **(3)** was also recovered from another red fraction in 30 to 50% yields. In the case of amines **(1d)** and **(1f)** the first eluted fraction was green. The products from these fractions were present in too small a quantity to allow a complete characterization; they were however purified by tlc on silica gel (petroleum ether/ethyl acetate 95/5) and the green spots then extracted with either chloroform **(1d)** or with benzene **(1f)**. These solutions gave intense ESR signals which were attributed to radicals **(10d)** and **(10f)** (see Table 3); mass spectra consistent with these two compounds were also obtained.

b) Reactions of 6c with 1c. Quinone-diimine **(6c)** (210 mg, 0.5 mmole) and p-anisidine **(1c)** (73 mg, 0.6 mmole) in 5 ml of CH_2Cl_2 were left at room temperature overnight. The solution was then evaporated to dryness and the residue chromatographed on a preparative silica gel tlc (cyclohexane/ethyl acetate 8:2). A red and a blue spot were obtained which afforded 120 mg of **9c** and 80 mg of unreacted **6c**.

c) Synthesis of bis(4-methoxyphenyl)amine, 1a. Bis(4-methoxyphenyl)nitroxide[22] (2g) and 0.7 g of iron powder were gently refluxed in 10 ml of AcOH; after cooling, the mixture was filtered, and the filtrate evaporated to dryness. The residue was taken up with benzene (40 ml) and shaked with 40 ml of a 10% aqueous solution of $NaHCO_3$. The benzene layer was dried over anidrous sodium sulphate and chromatographed through a short silica gel column (benzene/acetone 9/1). 1.45 g of **1a** (m.p. 104 C, literature[23] 102 C) were so obtained (77% yield).

d) ESR measurements. Compounds **5a-f**, **8c-e**, **10d** and **10f** were dissolved either in benzene or in chloroform and the solutions carefully deoxygenated by prolongued nitrogen bubbling. All spectra were recorded at room temperature on a Bruker ER-200-D X-band ESR spectrometer, equipped with an ASPECT 2000 dedicated computer, an NMR gaussmeter (Bruker) for field calibration and a Systron Donner frequency counter for the determination of g-factors.

Crystal structure of 2.2-diphenyl-4-(p-methoxyphenylamino)-5-(p-methoxyphenylimino)indolin-3-one N-oxide (9c).

e) i - X-ray structure analysis. **9c** crystallized from ethanol as deep red prisms. Lattice constants were determined repeatedly rectifing on the diffractometer the values of $(\vartheta, \chi, \varphi)h,k,l$ angles by twentyfive reflections to have the maximum of the peak when the angles were moving by 0.01° as a maximum.

Crystal data: $C_{34}H_{27}N_3O_4$, M = 541.6; monoclinic, a = 20.572(3), b = 8.180(1), c = 16.360(2)Å; β = 93.8(1)°, U = 2747.0(7)$Å^3$; Z = 4; D_c = 1.31 g cm^{-3}; Cu-$K\alpha$ radiation, λ =

1.5418Å; μ(Cu-K_α) = 6.6 cm^{-1}. Space group $P2_1/n$ (C_{2h}^5), from systematic absences. Intensity data were collected at 295K on a Siemens AED single-crystal diffractometer in the range 3° ⩽ ϑ ⩽ 70° using Ni-filtered Cu-K_α 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 ϑ-2ϑ step scanning mode using a scan width from (ϑ-0.60)° to (ϑ+ 0.60 + 0.142 tg ϑ)°. The intensities I_{hkl} were determined by analyzing the reflection profiles.[24] 5246 indipendent reflections were measured, 2909 of which were used in the crystal analysis having $I_{hkl} \geqslant 2\,\sigma(I_{hkl})$, $\sigma(I_{hkl})$ being based on statistic counting. One standard reflection was measured every 50 collected reflections to monitor crystal decomposition and instrumental linearity. Intensities I_{hkl} were corrected for Lorentz and polarization effects. The dimensions of the crystal were 0.24 x 0.57 x 0.24 mm (x,y,z). No absorption corrections were applied.

ii - Structure analysis and refinement. The structure was solved by direct methods using a system of computer programs,[25] and refined by a few cycles of full-matrix anisotropic least-squares up to R 0.074. A difference-Fourier synthesis computed at this stage revealed significant peaks near the positons where all the hydrogen atoms were expected to be. All the atomic parameters were then refined with full-matrix least-squares cycles, the weighting function being of the form $1/\omega = \sigma^2(F_o) + 0.005\,F_o^2$. The final agreement factor R was 0.039 and R_ω 0.038. The atomic scattering factors for oxygen[26], nitrogen[26], carbon[26] and hydrogen[27] were taken from the literature.

All calculations were carried out on a CRAY X-MP/12 computer, 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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