PERKIN 2

Radical cations: reactions of 2-phenylindole with aromatic amines under anodic oxidation. β-Scission of an amino alkoxy radical

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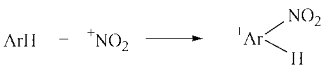
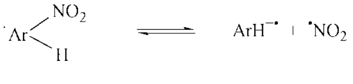
2-Phenyl-1*H*-indole reacts with *p*-anisidine, 2-nitro-*p*-anisidine and 2-nitro-*p*-methylaniline, under anodic oxidation, to give several products, depending on the potential used and on the presence or the absence of oxygen and a deprotonating agent. This investigation gives new insights into the reactivity of radical cations generated by a controlled anodic potential and neutral radicals corresponding to either 2-phenyl-1*H*-indole or to the three amines studied. The chosen amines show oxidation potentials lower (*p*-anisidine), equal (2-nitro-*p*-anisidine) or higher (2-nitro-*p*-methylaniline) than that of 2-phenyl-1*H*-indole and the reactions were carried out at the potential of the studied compounds. The oxidation of 2-phenyl-1*H*-indole in oxygen affords a new indole derivative, whose formation has been explained by β-scission of an indol-2-yloxyl radical and its structure was confirmed by X-ray analysis.

Radical cations may be easily generated from substrates with relatively low oxidation potentials by chemical[1] and electrochemical[2] oxidation and by reactions involving electron transfer processes.[3] In our opinion, many reactions interpreted by an electron transfer process actually occur through an ionic mechanism, whereas others described by an ionic mechanism, involve an electron transfer process. The wrong interpretation may be attributed to the complex reactivity of radical cations, which has recently been described in an excellent review.[4] Some nitrations of aromatic hydrocarbons, one of the classical electrophilic aromatic substitution reactions,[5] on the basis of radical cation formation and of side-products originating from typical oxidation processes, have been interpreted as occurring by an outer-sphere electron transfer mechanism, even though this did not agree with the experimental results and theoretical treatment.[6] In fact, these reactions were subsequently explained by an inner-sphere electron transfer mechanism as shown in eqns. (1) and (2).



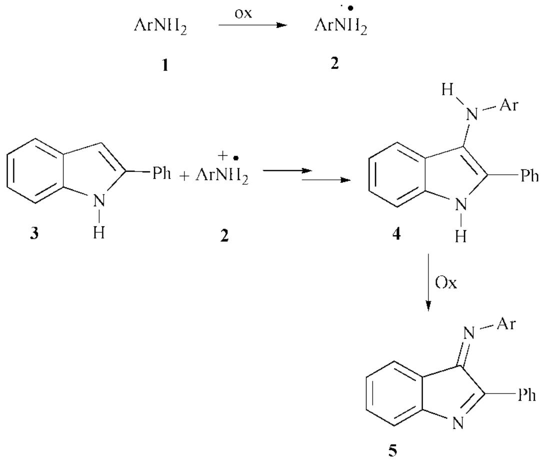
(1)



(2)

Another similar example has been recently observed by us in the reaction of indoles with nitrosoarenes in the presence of acids. In this case too, the redox potentials of the reactants cannot justify an outer-sphere electron transfer and thus, the formation of the phenylaminoxyl (reaction with nitrosobenzene) detected for the reaction carried out in the EPR cavity, could be more likely explained through an inner-sphere electron transfer.[7] Instead, the reactions of quinoline *N*-oxide with primary alkyl Grignards, such as hex-5-enylmagnesium bromide, for which a mechanism involving an outer-sphere electron transfer was proposed,[8] indeed take place through the classical nucleophilic addition.[9]

Years ago we studied the reactions of primary aromatic amines with 2-phenyl-1*H*-indole in the presence of oxidants such as lead tetraacetate,[10] *N*-chloroisatin,[10] N^1-chlorobenzotriazole,[10] and (diacetoxyiodo)benzene,[11] where direct amination of 2-phenyl-1*H*-indole was observed. All these oxidants are able to oxidise primary aromatic amines with an oxidation potential ranging between 0.25–1.0 V *vs.* Ag/AgClO$_4$ in CH$_3$CN as shown in Scheme 1.[12]



Scheme 1

On this basis, the formation of compound **5** could have been explained by the reaction sequence shown in Scheme 1. Since some aromatic amines anodically oxidised in the presence of 2-phenyl-1*H*-indole did not give compound **5**,[10] the reaction described in Scheme 1 was interpreted by the intermediate formation of a nitrenium ion as shown in eqn. (3).

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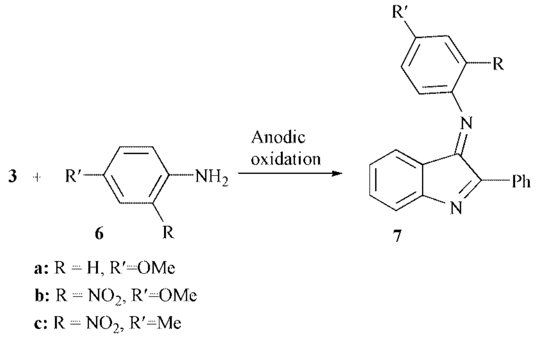
$$\mathrm{Ar{-}NH_2} \xrightarrow{\mathrm{OX}} \mathrm{Ar{-}NH{-}X} \rightleftharpoons \mathrm{Ar{-}\overset{+}{N}H} + \mathrm{X^-} \qquad (3)$$

In fact, primary aromatic amines may react with the oxidants mentioned affording the intermediate ArNHX (X = acetate or chloride anions) (eqn. (3)), which, according to the literature reports,[13] decomposes in the reaction medium to give the nitrenium ion. This attacks nucleophiles which leads to products of direct amination. The mechanism involving the nitrenium ion is also supported by the reactions of nitrosoarenes in the presence of acid, which give products **5** in good yields.[14]

The above data demonstrate that the mechanism of the reactions of radical cations of primary aromatic amines towards nucleophiles must not be taken for granted. The aim of this work was to study the role of amino radical cations in the direct amination of 2-phenyl-1*H*-indole under anodic oxidation, using primary aromatic amines with appropriate oxidation potentials.

Results

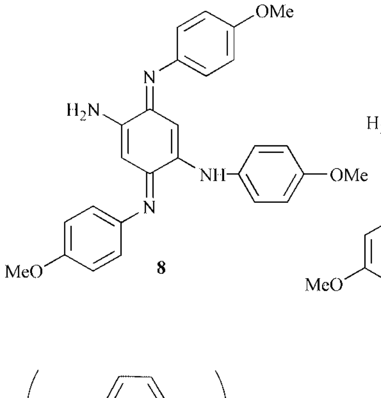
Cyclic voltammetry of 2-phenyl-1*H*-indole **3** shows an irreversible monoelectronic anodic wave with $E_{ox} = 0.74$ V. The cyclic voltammetry of the three chosen amines **6a–c** (Scheme 2) also shows an irreversible monoelectronic wave with $E_{ox} = 0.30$, 0.78 and 0.97 V, respectively. All the oxidation potentials are *vs.* Ag/AgClO$_4$ in CH$_3$CN (see below).



Scheme 2

Anodic oxidation of 3 with 6a

The reaction was performed at 0.3 V in the presence and in the absence of deprotonating agents: the electrolysis ends with the consumption of one electron per mole of amine. In both cases, 2-phenyl-1*H*-indole was recovered unchanged; only amine **6a** reacts, giving compounds **8**,[15] **9** and **10**[16] which were isolated and identified by comparison with authentic samples. Compound **8**, which has already been described,[15] shows spectroscopic data (reported here for the first time), which are in agreement with the proposed structure. Compounds **9** and **10** were identified by comparison with authentic samples, prepared by oxidising *p*-anisidine with lead dioxide: the latter reaction affords only compounds **9** and **10** (see the Experimental section). The reaction carried out in the presence of pyridine favours the formation of compounds **8–10**.



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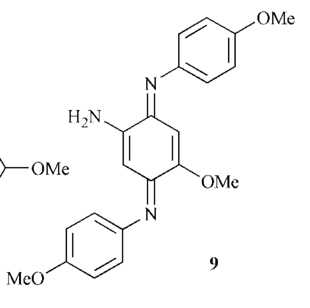

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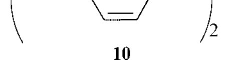

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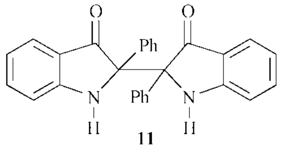
Anodic oxidation of 3 with 6b

The reaction was carried out at 0.78 V in the absence of deprotonating agents. The electrolysis goes to completion with consumption of two electrons per mole of amine. On working up the reaction, only the starting materials were recovered and no traces of the azo derivative or the expected product **7b** were detected. The same reaction performed in the presence of deprotonating agent led to the formation of compound **7b** as the main product, and small amounts of compounds **11–13**: the electrolysis in this case, consumed 2.7 electrons per mole of amine. Compound **7b** was identified by comparison with a sample obtained from an independent method.[10] Analytical data for compounds **11**,[17] **12**[18] and **13**[19] were compared with samples previously described.



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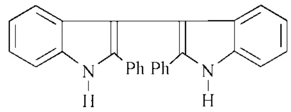

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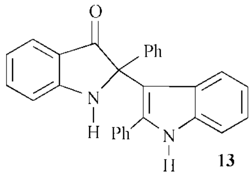

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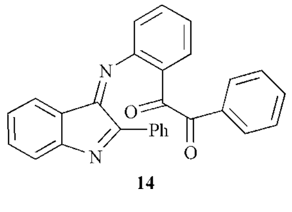
Anodic oxidation of 3 with 6c

The reaction carried out at 0.97 V was performed in the presence and in the absence of pyridine. In the absence of deprotonating agents only the starting amine was identified in the formed tar. The reaction carried out in the presence of pyridine led to the formation of small amounts of compound **13** together with the imino-derivative **7c**. The consumption of electrons for complete electrolysis was 4 electrons per mole of starting amine. Compound **7c** was identified by its spectroscopic data and by comparison with a sample appropriately prepared (see the Experimental section). Compound **13**[19] was identified by comparison with an authentic sample.

Anodic oxidation of 2-phenyl-1*H*-indole 3 with dioxygen

In order to understand the formation of indole dimers **11–13**, 2-phenyl-1*H*-indole **3** was anodically oxidised under N$_2$ and in the presence of oxygen. The experiment carried out at 0.85 V under nitrogen and in the presence of pyridine gave only small amounts of dimers **11** and **13**, together with a lot of starting material. The same experiment performed under air gave compound **14** as the main product, together with traces of **11**. Compound **14**, which shows spectroscopic data in agreement with the found structure, was identified by X-ray analysis (Fig. 1). After the current had fallen to its background value, *ca.* 1.2 F mol^{-1} of indole was observed in the absence of oxygen while *ca.* 2.3 F mol^{-1} were involved in the presence of oxygen.



14

Table 1 Selected bond distances (Å), angles (°) and torsion angles (°) with esd's in parentheses for compound **14**

N(1)–C(1)	1.304(5)	C(3)–C(8)	1.389(5)
N(1)–C(8)	1.428(5)	C(21)–C(22)	1.397(6)
C(1)–C(2)	1.517(5)	C(22)–C(27)	1.467(7)
C(1)–C(11)	1.473(5)	O(27)–C(27)	1.223(6)
N(2)–C(2)	1.272(5)	C(27)–C(28)	1.533(6)
C(2)–C(3)	1.477(6)	O(28)–C(28)	1.227(5)
N(2)–C(21)	1.419(5)	C(28)–C(281)	1.472(6)
C(1)–N(1)–C(8)	107.2(3)	N(1)–C(8)–C(3)	112.9(4)
C(2)–N(2)–C(21)	122.6(4)	N(2)–C(21)–C(22)	119.5(4)
N(1)–C(1)–C(2)	111.1(4)	C(21)–C(22)–C(27)	119.1(4)
C(1)–C(2)–C(3)	103.8(3)	O(27)–C(27)–C(28)	116.6(4)
C(2)–C(3)–C(8)	105.0(4)	O(28)–C(28)–C(27)	118.0(4)
N(1)–C(1)–C(2)–N(2)	3.9(4)	O(27)–C(27)–C(28)–O(28)	120.4(5)
N(2)–C(21)–C(22)–C(27)	−11.0(6)	O(28)–C(28)–C(281)–C(286)	10.8(7)
C(21)–C(22)–C(27)–O(27)	−40.9(6)		

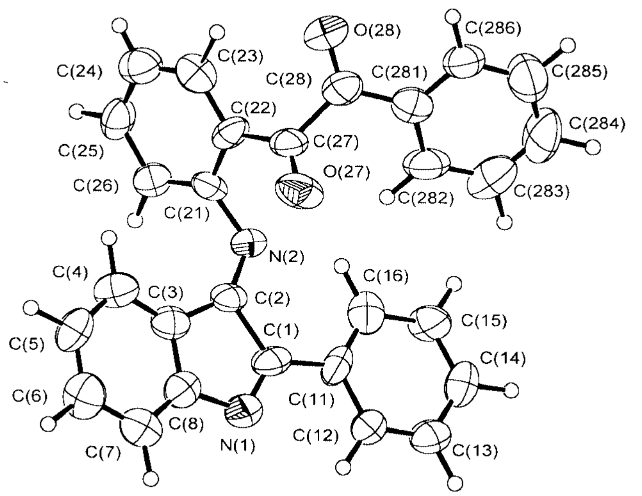


Fig. 1 ORTEP plot of compound **14** showing 50% probability displacement ellipsoids. H atoms are drawn as small circles of arbitrary radius.

Anodic oxidation of amines 6a–c

The anodic oxidation of **6a**, carried out at 0.3 V in the presence of a deprotonating agent, gave compounds **8**, **9** and **10**. The oxidation of amines **6b** and **6c**, performed at 0.8 and 1.0 V respectively, formed a tar and so did not allow the identification of products.

Electrochemical measurements

Voltammetric studies. Cyclic voltammetries of compounds **3** (2-phenyl-1*H*-indole) and **6a**–**c** (aromatic amines) were carried out at room temperature in a three-electrode cell containing nitrogen purged solutions of substrate (1×10^{-3} mol L^{-1}) in anhydrous MeCN–$NaClO_4$ (0.1 mol L^{-1}). Pyridine was used as a deprotonating agent. A static platinum electrode was used as a working electrode, a platinum wire as a counter electrode and Ag/$AgClO_4$ (0.1 mol L^{-1})–MeCN/fritted glass disk/$NaClO_4$ (0.1 mol L^{-1})–MeCN/fritted glass disk as a reference electrode.[20] The accuracy in potential values is ±5 mV. Unfortunately, the nonreproducibility of the cyclic voltammograms did not allow a quantitative evaluation for each reaction; this was certainly due to the deposit formed at the electrode during anodic oxidation.

Molecular geometry of 3-[2-(phenyldicarbonyl)phenyl]imino-2-phenyl-3*H*-indole 14

Selected bond distances, angles and torsion angles are reported in Table 1 and the arbitrary numbering scheme used in the crystal analysis is shown in Fig. 1, which represents a perspective view of the molecule.

The intramolecular bond lengths and angles, in line with the hybridisation expected for the atoms involved and in reasonable agreement with those reported in the literature for the 3*H*-indole[21] and for benzil[22–29] groups, show the presence of four localised double bonds: N(1)=C(1) 1.304(5) Å; N(2)=C(2) 1.272(5) Å confirming the iminic character of the N(2) atom; and C(27)=O(27) 1.223(6) and C(28)=O(28) 1.227(5) Å as expected for the carbonyl groups in benzil. In addition, the short distances involving N(1) and N(2) separated by the long C(1)–C(2) distance, 1.517(5) Å and the planar geometry of this part of the molecule [N(1)=C(1)–C(2)=N(2) torsion angle 3.9(4)°] suggest the possibility of a conjugative interaction between the p orbitals of the nitrogen atoms.

Regarding the geometry of the benzil moiety, only the *trans* conformation is known in the solid state and this is not usually planar. From the analysis of the torsion angles O=C–C=O and O=C–C(Ph)⎓C(Ph) reported in the literature, it seems that the most likely conformation is that in which the carbonyl is coplanar with its benzene ring, indicating that the probability of π interaction between the two carbonyls is minimal [O=C–C(Ph)⎓C(Ph) torsion angle −3.9° in ref. 16; −4.2° in ref. 18; 2.8° in ref. 18; −2.6° in ref. 20; −0.4, −1.6, −2.3, −19.4° in ref. 21; −1.6, 2.6, −3.1, 7.3° in ref. 22 and the corresponding O=C–C=O torsion angle 107.8; 108.4; −123.1; 122.5; 96.1 and 137.8; 109.5 and 111.6°, respectively]. When the steric hindrance of the benzene substituents prevents coplanarity, then the π interaction between the carbonyl groups is possible [O=C–C(Ph)⎓C(Ph) torsion angle −95.0° in ref. 23; 73.5 and 76.9° in ref. 24 with the corresponding O=C–C=O torsion angle 180.0 and −177.6°, respectively]. In our molecule, only the carbonyl containing O(28) can align with the plane of the adjacent benzene ring [O(28)=C(28)–C(281)–C(286) torsion angle 10.0(7)°] while O(27) is hindered by the iminic nitrogen [C(21)–C(22)–C(27)=O(27) torsion angle −40.9(6)°]. The torsion angle O(27)=C(27)–C(28)=O(28) is 120.4(5)°.

From the study of the molecular conformation, all the rings in the molecule are planar within experimental error: by denoting A and B the five- and the six-membered rings in the indole nucleus as A and B and the benzenes containing C(11), C(21) and C(281) as C, D and E, respectively, they form angles of A with B 2.9(1), B with C 5.7(1), B with D 72.4(1), D with E 41.6(1)°. Molecular packing is consistent with van der Waals interactions.

Discussion

In the review published by Schmittel and Burghart,[4] it is clearly demonstrated that the reactivity of radical cations cannot be explained through a simple and general mechanism. This work has been performed to understand the reactivity of radical cations of primary aromatic amines towards indoles and that of indoles towards primary aromatic amines in conditions in which radical cations are selectively produced. The choice of 2-phenyl-1*H*-indole was made because its direct amination affords compounds **7a**–**c** as the final products of the reaction, which are stable at the potential used during the electrolysis. The choice of amines **6a**–**c** was based on the fact that they show oxidation potentials which are lower (**6a**, 0.3 V), equal (**6b**, 0.78 V) or higher (**6c**, 0.97 V) than that of 2-phenyl-1*H*-indole (0.74 V).

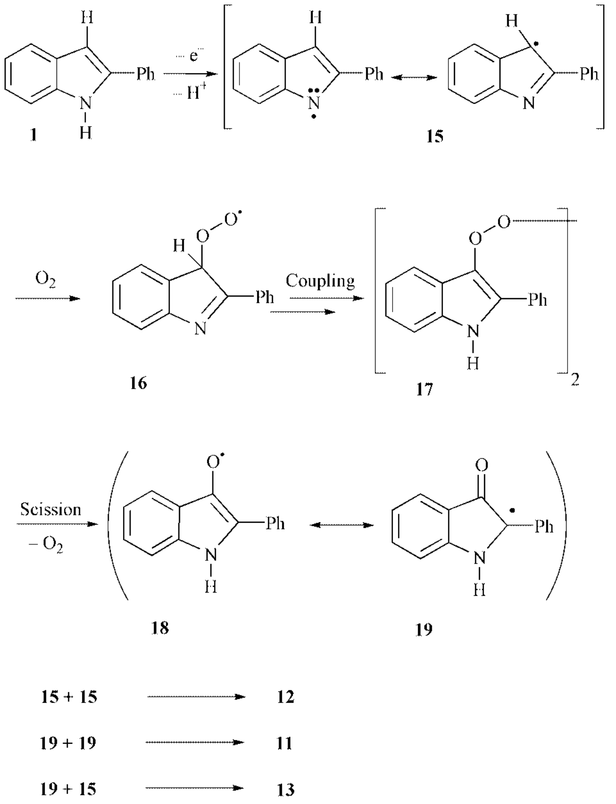
In the case of *p*-anisidine **6a** and at 0.30 V, the radical cation of the amine was produced in the presence of 2-phenyl-1*H*-indole **3** and no reaction was observed between these two species, even though **3** is a very good nucleophile.[30] The isolated products were compounds **8**–**10**. Since the formation of compounds **8**–**10** is favoured by the presence of a deprotonating agent, we suggest that they derive from the aminyl radical **6a**$^{\bullet}$ rather than from the radical cation **6a**$^{+\bullet}$. In the absence of a deprotonating agent, the formation of the aminyl radical may be promoted by the acid–base equilibrium shown in eqn. (4),

$$\mathrm{ArNH_2^{+\bullet} + ArNH_2 \rightleftharpoons ArNH^{\bullet} + ArNH_3^{+}} \qquad (4)$$

which could be shifted further to the right in this case, owing to the sufficiently higher basicity of amine **6a** with respect to the other studied amines. The results obtained in the case of amine **6a**, clearly show that both the radical cation **6a**$^{+\bullet}$ and the aminyl radicals are unable to attack the indole.

In the case of amine **6b** and at 0.78 V, the radical cations **3**$^{+\bullet}$ and **6b**$^{+\bullet}$ were both produced at the electrode. In the absence of deprotonating agents, the imino derivative **7b** was not formed demonstrating that radical cations **3**$^{+\bullet}$ and **6b**$^{+\bullet}$ cannot interact together. In the presence of pyridine, the imino derivative **7b** was the main product of the reaction. In both cases, the azo compound was never isolated. This result could be interpreted by assuming the deprotonation of both radical cations **3**$^{+\bullet}$ and **6b**$^{+\bullet}$ and the coupling of the two neutral radicals **3**$^{\bullet}$ and **6b**$^{\bullet}$. Other possibilities that cannot be ruled out are that the imino derivative **7b** could be formed by the interaction of **3**$^{+\bullet}$ with the aminyl radical **6b**$^{\bullet}$ or by reaction of the indolyl radical **3**$^{\bullet}$ with the radical cation **6b**$^{+\bullet}$. There are no experimental data or literature reports to strongly support any of the three proposed mechanisms, but if we also consider that the neutral radicals **3**$^{\bullet}$ and **6b**$^{\bullet}$ possess an electrophilic character,[31] their interaction could be favoured compared with that involving a neutral radical and a radical cation. That no azo compound was formed may be attributed to both steric hindrance of the nitro groups and to better delocalisation of the free electron in the aromatic ring of the aminyl radical **6b**$^{\bullet}$ compared with **6a**$^{\bullet}$. The formation of the oxygenated dimers could be explained as shown in Scheme 3. The indolyl radical **15**$^{\bullet}$ may react with oxygen at C-3[32] to form the peroxyl **16**, which dimerises to the corresponding tetraoxy compound[33–36] and then subsequently decomposes with oxygen elimination to give indolyloxyl radical **18**. This reacts with itself giving **11** or with **15** affording **13**. The dimer **12** clearly derives from the coupling of two molecules of **15**.

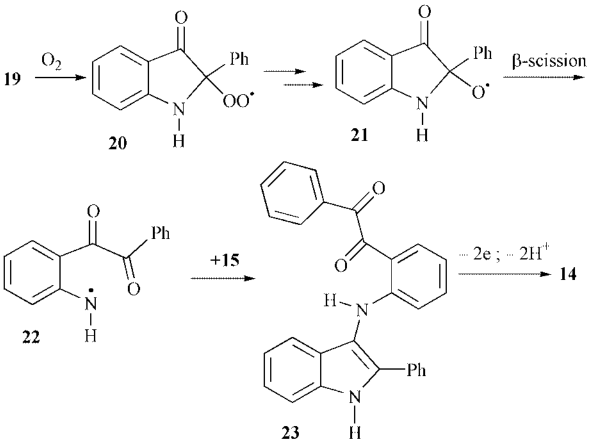
In the case of **6c** in which the reaction is carried out at 0.97 V there are no significant results in the absence of deprotonating agents, whereas products, which can give information on the reaction mechanism, were isolated in the presence of pyridine. In fact, in this case, compound **7c** and the oxygenated dimer **13** were isolated. These results once again demonstrate that the imino derivative **7c** is formed when both reagents are oxidised to the corresponding radical cations in the presence of deprotonating agents: thus the formation of compound **7c** does not involve radical cations, but takes place only when neutral radicals are generated. In this reaction, compounds **3** and **6c** were both oxidised, although at different rates, because the working electrode used had a surface of 12 cm^2.



Scheme 3

The anodic oxidation of **6a**, performed at 0.3 V in the presence of a deprotonating agent, gave compounds **8**–**10** which are the same products as those isolated in the reaction **3** with **6a**. This clearly confirms that **6a**$^{\bullet}$ cannot react with 2-phenyl-1*H*-indole. The oxidation of **6b** and **6c**, also performed in the presence of a deprotonating agent, does not allow the isolation of any product in the formed tar.

Finally, the anodic oxidation of 2-phenyl-1*H*-indole carried out in oxygen, affords compound **14**. The formation of this compound may be explained by the interaction of intermediate **19** (Scheme 4) with oxygen. In this case, through the classical evolution of peroxyl radicals, such as that depicted in Scheme 3, **20** leads to intermediate **21**. The latter, by β-scission, gives rise to the formation of aminyl radical **22**, which may couple with an indolyl radical **15** affording compound **14** after oxidation.



Scheme 4

Conclusions

Radical cations of primary aromatic amines are unable to attack nucleophiles such as 2-phenyl-1*H*-indole and the 2-phenyl-1*H*-indolyl radical cation does not react with primary aromatic amines. The interaction between 2-phenyl-1*H*-indole and primary aromatic amines may only occur through coupling of their neutral radicals. The 2-phenyl-1*H*-indolyl radical cation can dimerise as observed for tetrahydrocarbazoles,[37] but dimerisation is faster when it reacts *via* the indolyl radical. When the latter is formed, it rapidly reacts with oxygen affording the oxygenated dimers, compounds **11** and **13**. The electrolysis of **3** with relatively high concentrations of oxygen leads to the formation of compound **14** as the main product. The low yield of the reactions may be ascribed in part to the deposition of indole radical cations at the electrode and in part to the oligomerisation of amines, which usually occurs under anodic oxidation.

Experimental

Melting points are uncorrected and were measured with an Electrothermal apparatus. IR spectra were recorded in the solid state on a Nicolet Fourier Transform Infrared 20-SX spectrophotometer equipped with a Spectra Tech. "Collector" for DRIFT measurements. ^{1}H NMR spectra were recorded at room temperature in $CDCl_3$ solution on a Varian Gemini 200 spectrometer (TMS was taken as reference peak). Mass spectra were performed on a Carlo Erba QMD 1000 mass spectrometer, equipped with a Fisons GC 8060 gas chromatograph. Voltammetric experiments were performed with a three-electrode multipolarograph AMEL 472 coupled with a digital *x*/*y* recorder AMEL 863, while controlled potential electrolyses were carried out with an AMEL 552 potentiostat coupled with an AMEL 731 integrator and a LINSEIS L250E recorder.

2-Phenyl-3-(2-nitro-4-methoxyphenylimino)-3*H*-indole **7b**,[10] bis(4-methoxyphenyl)diazene **10**, 2,2′,3,3′-tetrahydro-3,3′-dioxo-2,2′-diphenyl-2,2′-bi-1*H*-indole **11**,[17] 2,2′-diphenyl-3,3′-bi-1*H*-indole **12**,[18] 2′,3′-dihydro-3′-oxo-2,2′-diphenyl-3,2′-bi-1*H*-indole **13**[19] and lead dioxide[38] were synthesised according to the literature. 2-Phenyl-1*H*-indole **3**, *p*-toluidine **6a**, 2-nitro-*p*-anisidine **6b** and 2-nitro-*p*-methylaniline **6c** were purchased from Aldrich and purified by crystallisation. $NaClO_4$ was dried under vacuum after crystallisation. Molecular sieves were added to anhydrous acetonitrile (Aldrich).

All solvents were Carlo Erba or Aldrich RP-ACS grade and were purified according to the literature.[39]

Electrochemical oxidation: general procedure

In analytical and large scale electrolyses a platinum gauze cylinder (area *ca.* 12 cm^2) was used as working electrode, while the auxiliary one was a platinum wire placed on the inner wall of a glass tube containing a $NaClO_4$ saturated acetonitrile solution and connected to the test solution *via* a methyl cellulose–DMF–$NaClO_4$ plug/sintered glass disk.

In a typical run, 60 mL of anhydrous MeCN–$NaClO_4$ (0.1 mol L^{-1}) containing 2-phenyl-1*H*-indole (0.6 mmol) and one of the amines **6a**–**c** (0.6 mmol) were electrolysed at the oxidation potential of the amine used. The solution was magnetically stirred and kept under a continuous nitrogen flow. All electrolyses were carried out in the absence and in the presence of a deprotonating agent: in this last case pyridine (6 mmol) was added to the electrolysed solutions. After the current had fallen to its background value, the solution was evaporated to dryness. The crude residue was treated with water (100 mL) and extracted with $CHCl_3$ (3 × 30 mL); the organic layer was dried (Na_2SO_4) and concentrated under vacuum. The residue was then chromatographed by preparative TLC using cyclohexane–ethyl acetate in an 8 : 2 ratio. The order of increasing R_f is reported below for each reaction. All the isolated fractions were analysed by spectroscopic methods.

Reaction 3 + 6a. (R_f): **8** < **9** < **3** < **10**. The R_f of compound **9** is about 0, so 5% Et_3N must be added to the above mentioned eluant (R_f becomes 0.3). Compound **8** had already been reported, but its characterization was limited to its melting point (163 °C).[40] Full spectroscopic data are reported below. Compounds **9** and **10** were identified by comparison with authentic samples.

*Compound **8***. Mp = 160–62 °C (from ethanol); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 3.78 (s, 3H), 3.81 (s, 3H), 3.84 (s, 3H), 5.08 (broad, 2H, disappears with D_2O), 5.78 (s, 1H), 6.12 (s, 1H), 6.85 (m, 10H), 7.07 (d, 2H, J = 8.4 Hz), 8.02 (broad, 1H, disappears with D_2O) ppm; IR (KBr): ν/cm^{-1} = 3474, 3336, 3255, 2925, 1605, 1456, 1377; M for $C_{27}H_{26}N_4O_3$, 454.52; MS (EI$^+$): m/z = 454 (100), 439 (18), 423 (17), 408 (22), 332 (18), 301 (15).

Reaction 3 + 6b. (R_f): **7b** < **13** < **12** < **11**. All the products have already been reported elsewere,[10,17–19] so only the mass spectra of the TLC fractions were performed.

*Compound **7b***. Yield = 25%; M for $C_{21}H_{15}N_3O_3$, 357.36; MS (EI$^+$): m/z = 359 (22), 357 (4), 327 (100), 312 (31), 208 (40).

*Compound **11***. Yield = traces; M for $C_{28}H_{20}N_2O_2$, 416.46; MS (EI$^+$): m/z = 209 (29), 207 (31), 179 (100), 152 (24), 104 (17).

*Compound **12***. Yield = traces; M for $C_{28}H_{20}N_2$, 384.46; MS (EI$^+$): m/z = 384 (75), 307 (8), 280 (12), 192 (11).

*Compound **13***. Yield = traces; M for $C_{28}H_{20}N_2$, 400.46; MS (EI$^+$): m/z = 400 (54), 384 (21), 371 (34), 309 (30), 295 (21), 193 (58).

Reaction 3 + 6c. (R_f): **7c** < **13**. The dimer **13** and compound **7c** were identified by comparison with authentic samples. The yield was 43% for **7c**, while only traces of compound **13** were detected.

Synthesis of compound 7c

N^1-Chlorobenzotriazole (4 mmol), dissolved in CH_2Cl_2 (10 mL) was added dropwise to a solution of 2-phenyl-1*H*-indole (1 mmol) and 2-nitro-*p*-methylaniline (2 mmol) in CH_2Cl_2 (30 mL). After 2 h the mixture was poured into 10% aqueous $NaHCO_3$ and the organic layer was washed with water (2 × 20 mL), dried (Na_2SO_4) and concentrated to dryness. The residue was chromatographed on a silica gel column (eluant cyclohexane–ethyl acetate 7 : 3) and the obtained compound **7c** was crystallised from methanol. Yield = 40%; mp = 194–195 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 2.52 (s, 3H), 6.58 (d, 1H, J = 8.2 Hz), 6.90 (d, 1H, J = 8.2 Hz), 6.94 (td, 1H, J = 7.4 and 1.0 Hz), 7.48 (m, 6H), 8.10 (s, 1H), 8.40 (d, 1H, J = 8.1 Hz), 8.41 (d, 1H, J = 7.0 Hz) ppm; IR (KBr): ν/cm^{-1} = 3050, 2945, 1641, 1560, 1519, 1450, 1342, 762, 688; M for $C_{21}H_{15}N_3O_2$, 341.36; MS (EI$^+$): m/z = 341 (5), 325 (4), 311 (100), 295 (4), 281 (6), 205 (14), 179 (20), 152 (16).

Synthesis of compounds 9 and 10

Amine **6a** (0.2 g, 1.6 mmol) was dissolved in benzene (40 mL) and activated lead dioxide (0.7 g, 3.0 mmol) was added. After 5 h the mixture was filtered and the filtrate evaporated to dryness. The residue was chromatographed on a silica gel column (eluant cyclohexane–ethyl acetate 8 : 2 with 0.5% of Et_3N). Both **9** and **10** were crystallised from absolute ethanol.

Compound 9. Yield = 46%; mp = 218–219 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 3.72 (s, 3H), 3.82 (s, 3H), 3.84 (s, 3H), 4.93 (br, 2H, disappears with D_2O), 5.82 (s, 1H), 6.00 (s, 1H), 6.90 (m, 8H) ppm; IR (KBr): ν/cm^{-1} = 3458, 3282, 2966, 1602, 1442, 829; M for $C_{21}H_{21}N_3O_3$, 363.41; MS (EI$^+$): m/z = 363 (100), 346 (50), 332 (44), 303 (26), 226 (17).

Electrochemical oxidation of 2-phenyl-1*H*-indole 3

Controlled potential electrolyses of 2-phenyl-1*H*-indole [0.6 mmol in 60 mL of MeCN–$NaClO_4$ (0.1 mol L^{-1})] were carried out in the same medium and using the same apparatus, in the absence and in the presence of pyridine as deprotonating agent. Experiments were carried out under a continuous nitrogen flow

Table 2 Experimental data for the X-ray diffraction studies on crystalline compound **14**

Formula	$C_{28}H_{18}N_2O_2$
Formula weight	414.5
Crystal system	Triclinic
Space group	$P\bar{1}$
Cell parameters at 295 K	
a/Å	9.093(2)
b/Å	14.257(3)
c/Å	8.389(2)
α/Degree	93.42(5)
β/Degree	107.21(5)
γ/Degree	84.84(5)
V/Å^3	1034.0(5)
Z	2
d_{calc}/g cm^{-3}	1.33
Crystal dimensions/mm	0.34 × 0.28 × 0.48
Linear absorption coefficient/cm^{-1}	6.7
Unique total data	3921
Criterion of observation	$I > 2\sigma(I)$
Unique observed data (NO)	1841
No. of refined parameters (NV)	361
Overdetermn ratio (NO/NV)	5.1
R [b]	0.051
R_w [c]	0.059
GOF [d]	0.749
Largest shift/esd	0.850
Largest peak/e Å^{-3}	0.174
Programs	[a]

[a] SIR97,[41] SHELX76,[42] PARST.[43] [b] $R = \Sigma|\Delta F|/\Sigma|F_o|$. [c] $R_w = [\Sigma w(\Delta F^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$. [d] $GOF = [\Sigma w|\Delta F|^2/(NO - NV)]^{1/2}$.

and in the presence of dioxygen, bubbled into the test solution throughout the electrolysis. The reaction in the presence of nitrogen was worked up as described above, and traces of compounds **11** and **13** were identified.

The crude residue of the electrolysis in the presence of oxygen was poured in water (100 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The organic layer was dried with Na_2SO_4, concentrated to dryness and chromatographed on a column of silica gel using cyclohexane–ethyl acetate 8:2 as an eluant. Products were eluted in the order of R_f: **14** < **11** (traces).

Compound 14. Yield = 21%; mp = 139–141 °C (CH_2Cl_2); ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 6.42$ (d, 1H, $J = 7.4$ Hz), 6.92 (m, 2H), 7.08 (t, 2H, $J = 7.6$ Hz), 7.42 (m, 9H), 7.69 (td, 1H, $J = 7.7$ and 1.4 Hz), 8.10 (dd, 2H, $J = 8.4$ and 1.5 Hz), 8.20 (dd, 1H, $J = 7.9$ and 1.3 Hz) ppm; IR (KBr): ν/cm^{-1} = 3061, 2924, 1678, 1608, 1465, 1354, 758; M for $C_{28}H_{18}N_2O_2$, 414.44; MS (EI$^+$): m/z = 414 (7), 309 (100), 281 (10), 207 (12), 179 (42).

Electrochemical oxidation of aromatic amines 6a–c

Controlled potential electrolyses of amines **6a**–**c** [0.6 mmol in 60 mL of MeCN–$NaClO_4$ (0.1 mol L^{-1})] were carried out in the same medium and using the same apparatus (see above), in the absence and in the presence of pyridine as a deprotonating agent, under a continuous nitrogen flow. In the case of *p*-anisidine, triethylamine (0.1 mol L^{-1}) was also used as a stronger deprotonating agent. In all the cases reported above, after the current had fallen to its background value, the solution was evaporated under vacuum and the residue was treated as described above. In the case of **6a**, operating in the presence or in the absence of a deprotonating agent, compounds **8**–**10** were isolated and identified as described above for the reaction of **3** with **6a**. Under the same conditions, the oxidation of amines **6b** and **6c** did not give appreciable amounts of products.

Crystal structure of 3-[2-(phenyldicarbonyl)phenyl]imino-2-phenyl-3*H*-indole 14

Table 2 shows the experimental and crystallographic data. The intensities I_{hkl} were determined by analysing the reflection profiles by the Lehmann and Larsen[44] procedure. Corrections for Lorentz and polarisation effects were performed; there were no corrections for absorption effects.

Atomic scattering factors were from the International Tables for X-Ray Crystallography.[45] Bibliographic searches were carried out using the Cambridge structural database files through the Servizio Italiano di Diffusione Dati Cristallografici, Parma, Italy.†

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