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Oxidative trimerization of indole: on the formation of dications and radical cations by reaction of indole and nitrosobenzene in the presence of acids

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The reactions of indole with nitrosobenzene in the presence of acetic, monochloroacetic, monobromoacetic and trichloroacetic acid afford as the main product a deep-green precipitate, which in a preceding study had been erroneously identified as the aminyl radical of a trimer indole. The identity of the minor products was confirmed. This paper deals with the determination of the correct structure of the compounds contained in the precipitate through a study based on chemical reactions, electrochemical measurements and X-ray analysis.

We have previously observed that indole reacts with nitroso arenes in methylene chloride at room temperature and in the presence of monochloroacetic acid affording a deep-green precipitate as the main product. On the basis of its mass and EPR spectra this precipitate was initially described as an aminyl radical of a trimer indole.[1] Further studies on the green precipitate prompted by the finding that it exhibited semiconducting properties,[2] showed that it did not consist of a single product, being instead a mixture of a trimer indole radical cation and of a dication. The present paper mainly reports on new studies aimed to a full characterisation of the deep-green precipitate.

Results and discussion

The reaction of indole with nitrosobenzene, previously carried out in the presence of monochloroacetic acid,[1] was repeated using acetic, monobromoacetic and trichloroacetic acid in order to prepare salts with different solubility, to facilitate their identification by elemental analysis and to obtain crystals suitable for X-ray analysis (Scheme 1). In each of the reactions, compounds **3**–**7** were isolated as minor products and were characterised by comparison with those already described and accounted for in the previous study.[1]

The deep-green precipitate proved difficult to study, due to its insolubility in almost all solvents, including water, independently of the counter anion (the acid used); when it did dissolve in a solvent, as was the case for DMSO, it became colourless. The isolated precipitate was not a single compound but consisted of the radical cation **8** and the diamagnetic dication **9** in a ratio depending on the acid used and on the reaction conditions, *e.g.* stirring or not stirring the reaction mixture, varying the temperature or the nature of the solvent, *etc.* This mixture of **8** and **9** shows a very intense EPR signal resulting from the overlapping of two lines (see the *g*-factors in Table 1) which, due to its intrinsic asymmetry, may be attributed to two isomeric forms of radical cation **8**.

Table 1 *g*-Factors of the two isomeric forms (**I** and **II**) of the radical cations **8a**–**f**

	I	**II**
8a	2.0025(4)	2.0028(5)
8b	2.0024(8)	2.0028(4)
8c	2.0026(5)	2.0028(7)
8d	2.0026(0)	2.0028(0)
8e	2.0021(0)	—
8f	2.0025(9)	—

The colourless compound obtained upon dissolution of the green precipitate was identified as the reduced trimer **7**. This product, which has already been obtained by other investigators,[3–5] can actually be viewed as a precursor of both **8** and **9**. Indeed, compound **7** was converted to a mixture of **8b** and **9b** by oxidation with nitrosobenzene in the presence of monochloroacetic acid. In each of the reactions, the ratio between **8** and **9** was determined by treating the green precipitate with 4-aminopyridine suspended in dichloromethane; in this way, the two salts are quantitatively transformed into the trimer **7** and its oxidised form **10**, respectively. The ratios between these two species, which must be the same as those between **8** and **9**, were determined by HPLC and were found to be similar to those obtained from the elemental analyses of all the precipitated salts (see Experimental section).

Compound **7** could also be oxidised with iodine (1 : 0.5 molar ratio) in dichloromethane affording an EPR-active (single line, $g = 2.0021$) green–blue precipitate consisting of a mixture of **8e** and **9e** in a 1 : 1 molar ratio (as determined through elemental analysis). This suggests that the previous report[5] on the electro-oxidation of indole **1** in the presence of iodine needs to be reconsidered.

The mixture of **8** and **9** was reduced almost quantitatively, irrespective of the counter anions, by phenylhydrazine to

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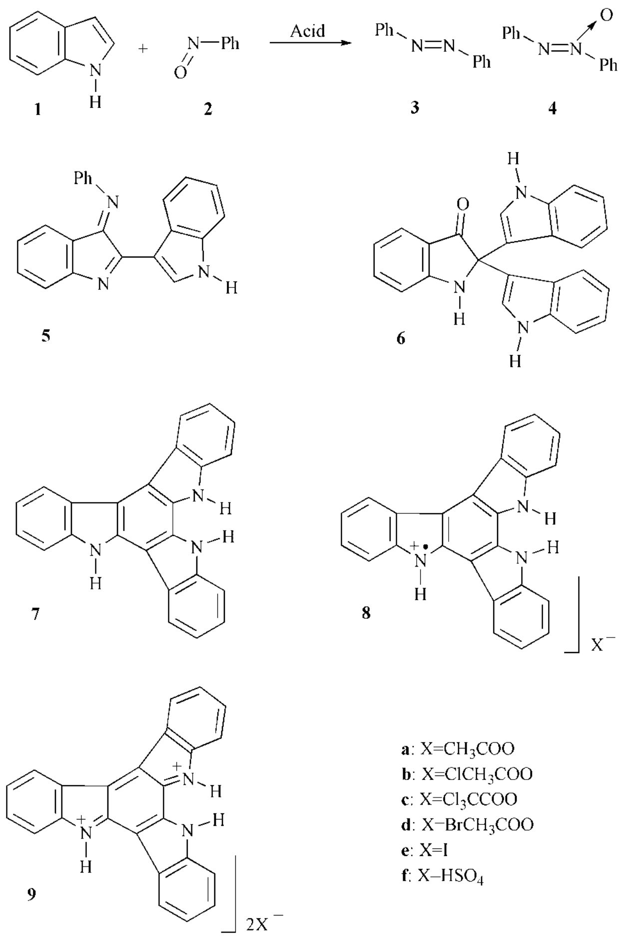
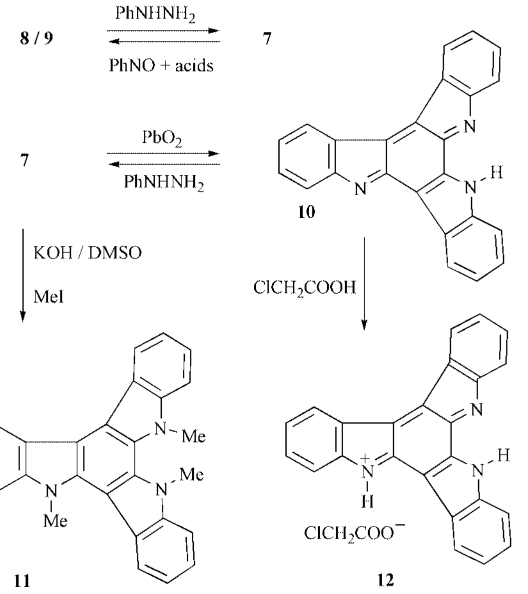


Scheme 1

compound **7** which, in turn, could be reoxidised to the quinonediiminic-like compound **10** by lead dioxide. Dissolution of compound **7** in sulfuric acid afforded a green solution exhibiting an EPR spectrum consisting of a single line that could not be resolved under any conditions and that was attributed to radical cation **8f**. The reversible transformation between **7** and **10** as outlined in Scheme 2, was also observed in the electrochemical study described in the following section. The structure of **10** is consistent with the fact that this compound could be reduced with potassium *tert*-butoxide in DMSO to its radical anion $\mathbf{10}^{-\bullet}$, whose EPR consists again of a single unresolved line ($g = 2.0026$).



Scheme 2

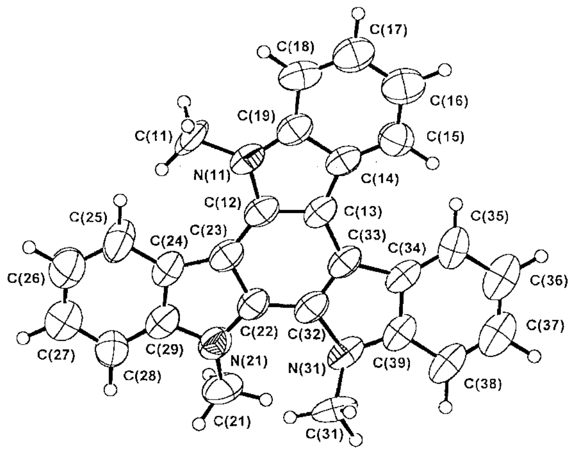


Fig. 1 ORTEP plot of compound **11** showing 50% probability displacement ellipsoids. H atoms are drawn as small circles of arbitrary radii.

Because of the aforementioned ability of nitrosobenzene to oxidise **7** under acidic conditions, it has been suggested that the reaction of indole **1** with nitrosobenzene **2** in the presence of acids first affords compound **7**, which is subsequently oxidised to **8** and **9** by the protonated nitrosobenzene.[6]

All compounds **7**–**10** were obtained in the crystalline state, but in no case were the crystals suitable for X-ray analysis. In order to by-pass this inconvenience, the methylated derivative **11** was prepared from **7**.[1] In this case the crystals could be used for X-ray analysis, which confirmed the assigned structure (Fig. 1).

With the aim of obtaining an authentic sample of compound **9b**, **10** was reacted with monochloroacetic acid in methylene chloride for 24 h. Unexpectedly, a brown precipitate was isolated which was identified by its elemental analysis as the salt **12**; this result can be attributed to the high insolubility of salt **12**.

Treating an equimolar methylene chloride solution of **7** and **10** with excess monochloroacetic acid afforded a green–blue precipitate exhibiting two overlapping, intense and unresolved EPR lines. The elemental analysis of the precipitate fitted with the expected comproportionation product **8b**.

Electrochemical measurements

With the aim of establishing the reversibility of the oxidation and reduction of compounds **7** and **10**, their electrochemical behaviour was studied in aprotic and protic media. Additional experiments were carried out using a modified UV cell in order to characterise the species being formed through their absorption spectra.

The cyclic voltammetry of **7** carried out from 0.0 V to 1.3 V in anhydrous DMF (aprotic medium), exhibited two monoelectronic anodic peaks, their potential values being respectively $E'_{\mathrm{ap}} = 0.67$ V and $E''_{\mathrm{ap}} = 1.20$ V (see Fig. 2, solid line). The cyclic voltammetry of **10**, carried out from 0.0 V to −0.8 V in the same medium, exhibited two monoelectronic cathodic peaks, with potential values $E'_{\mathrm{cp}} = -0.22$ V and $E''_{\mathrm{cp}} = -0.68$ V, respectively (see Fig. 3, solid line). The two-step reduction of **10** in the aprotic medium yields the corresponding radical anion and dianion. The cyclic voltammetry of **10** was also carried out in the presence of increasing amounts of protonating agents of different strength. As expected, both cathodic peaks shifted to a less negative potential, the second one merging with the first (see Fig. 3, dotted line). When cyclic voltammetries of compounds **7** and **10** were carried out from 0.0 V to 1.3 V, both in the presence of the same amount of trichloroacetic acid, their electrochemical behaviours were very similar, as shown

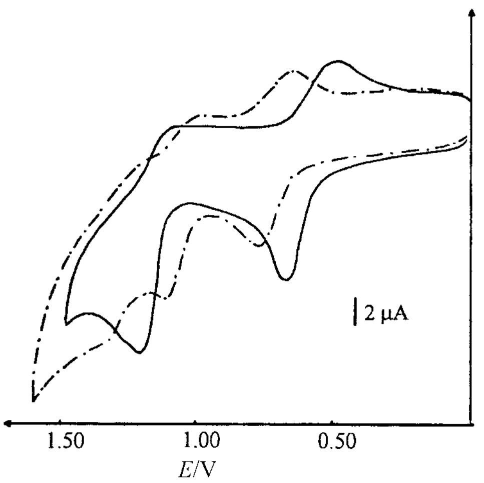


Fig. 2 Cyclic voltammetry of compounds **7** (solid line) and **11** (dotted line) 5.0 × 10^{-4} mol L^{-1} in anhydrous DMF containing $\mathrm{Bu^t_4NBF_4}$ (0.1 mol L^{-1}) at a GC electrode *vs.* $\mathrm{SCE_{(DMF)}}$,[20] sweep rate 0.200 V s^{-1}.

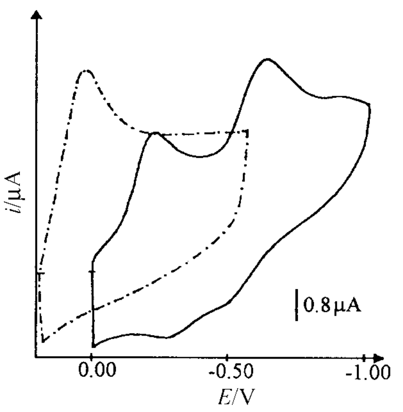


Fig. 3 Cyclic voltammetry of compounds **10** 3.0 × 10^{-4} mol L^{-1} in anhydrous DMF (solid line) and in the presence of monochloroacetic acid 9.0 × 10^{-4} mol L^{-1} (dotted line), 0.1 mol L^{-1} $\mathrm{Bu^t_4NBF_4}$ at a GC electrode, *vs.* $\mathrm{SCE_{(DMF)}}$,[20] sweep rate 0.200 V s^{-1}.

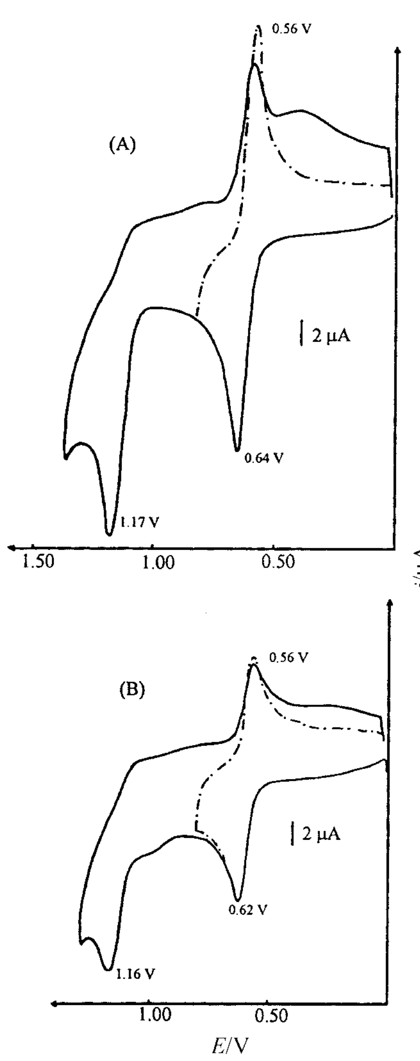


Fig. 4 Cyclic voltammetry of compound **7** (A) and **10** (B) (5.0 × 10^{-4} mol L^{-1}) in anhydrous DMF containing $\mathrm{Bu^t_4NBF_4}$ (0.1 mol L^{-1}) at a GC electrode *vs.* $\mathrm{SCE_{(DMF)}}$[20] in the presence of trichloroacetic acid *ca.* 1.0 × 10^{-3} mol L^{-1}, sweep rate 0.200 V s^{-1}.

in Fig. 4. The similar voltammograms and the peak potential values suggest that the protonated form of **10** is the dication of **7**, under these conditions the former species being readily reduced to **7** at the starting potential (0.0 V).

It is worth noting that in the case of **7** and only for a switching potential 1.3 V, two cathodic peaks appear (see Fig. 4 (A), solid line), the less positive and broadened one being probably due to a radical cation generated by electron transfer between the electrogenerated dication and the substrate **7**. In the case of **10**, where comproportion may not occur, only the reduction peak of the electrogenerated radical cation appears (see Fig. 4 (B), solid line).

The electrochemical behaviour of compound **11** in an aprotic medium was also studied. The cyclic voltammogram obtained (see Fig. 2, dotted line) was similar to that of the parent compound **7**, except for the presence of a third anodic peak corresponding to the oxidation of the third nitrogen atom, a process easier in **11** than in **7** owing to the electron donating effect of the methyl group.

To further support the possibility of interconversion of compounds **7** and **10**, the cathodic reduction of **10** was carried out in a weakly protic medium using a modified UV cell equipped for *in situ* electrolysis. The UV spectra of compounds **7** and **10** (see Fig. 5 (A)) recorded in the same medium were characteristic and different enough to evidence the occurrence of interconversion of the two species.

The UV spectrum of a totally electrolysed solution of **10** proved identical in shape to that of compound **7**, although with slightly shifted adsorbance values. When a stronger protonating agent like acetic acid was added to the same electrolysed solution, a blue shift led to complete overlapping of the spectra of **10** and **7** (see Fig. 5 (B)).

As it might have been foreseen, the UV spectrum of compound **11** (see Fig. 5 (A)) recorded in the same medium was very similar to that of compound **7**, but slightly red shifted.

Molecular geometry of 1,2,7-trimethyl-2,7-dihydro-1*H*-diindolo[2,3-*a*:2,3-*c*]carbazole, 11

As already mentioned, the X-ray crystallographic analysis of **11** was carried out in order to obtain a deeper insight of the structure(s) of **7** (and related compounds) that could not be obtained in a form suitable for X-ray studies. The geometrical parameters of the molecule are in good agreement with those expected from the hybridisation of the atoms. Bond distances and angles are reported in Table 2, and the arbitrary numbering scheme used in the crystal analysis is shown in Fig. 1 which represents a perspective view of the molecule.

The molecule as a whole cannot be considered fully planar, some deviations from coplanarity being observed in particular as far as the central benzene ring is concerned. For this ring, a quantitative evaluation of the deformation derived from the puckering coordinates[7] displays a half-boat conformation and in terms of asymmetry parameters[8] evidences a pseudo symmetry plane through atom C(12). The other benzene rings are planar within the experimental errors.

Table 2 Bond distances (Å) and angles (°) with esd's in parentheses for compound **11**

	X = 1	X = 2	X = 3
(a) In indole moieties			
N(X1)–C(X1)	1.447(8)	1.471(7)	1.459(6)
N(X1)–C(X2)	1.397(5)	1.373(6)	1.412(6)
N(X1)–C(X9)	1.364(6)	1.370(7)	1.382(6)
C(X2)–C(X3)	1.407(7)	1.424(6)	1.374(6)
C(X3)–C(X4)	1.418(6)	1.460(7)	1.443(7)
C(X4)–C(X9)	1.409(7)	1.399(6)	1.399(6)
C(X2)–N(X1)–C(X9)	109.1(3)	109.3(4)	106.0(4)
N(X1)–C(X2)–C(X3)	106.7(4)	109.5(4)	109.5(4)
C(X2)–C(X3)–C(X4)	109.1(4)	104.7(4)	108.1(4)
C(X3)–C(X4)–C(X9)	105.2(4)	107.2(4)	104.9(4)
N(X1)–C(X9)–C(X)4	109.9(4)	109.1(4)	111.3(4)
(b) In the central benzene moiety			
C(12)–C(23)	1.409(6)	C(22)–C(32)	1.394(7)
C(13)–C(33)	1.430(6)	C(12)–C(13)–C(33)	117.5(4)
C(13)–C(12)–C(23)	124.4(4)	C(12)–C(23)–C(22)	115.9(4)
C(23)–C(22)–C(32)	119.9(4)	C(13)–C(33)–C(32)	118.4(4)
C(22)–C(32)–C(33)	123.2(4)		

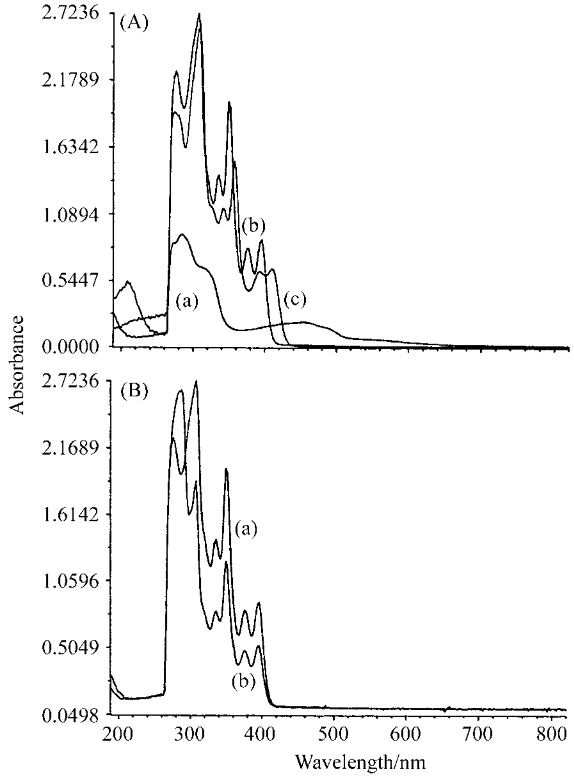


Fig. 5 (A) UV spectra of compounds **10** (a), **7** (b) and **11** (c) in anhydrous DMF containing Bu$^t_4$NBF$_4$ (0.1 mol L^{-1}) at a concentration of *ca.* 5.0 × 10^{-4} mol L^{-1}; (B) UV spectrum of compound **7** (a) and the product of the cathodic reduction of **10** (b) in the same conditions as (A) but in the presence of acetic acid.

The analysis of the planarity indicates that all the five membered rings can be considered planar. Actually, the ring containing N(11) is strictly planar and also the coordination geometry at N(11) is trigonal planar [the sum of the valence angles involving N(11) is 359.9° and the distance out of plane of C(11) is 0.063(7) Å]. On the other hand, the minimal distortions from coplanarity observed for the pyrrole rings containing N(21) and N(31) and especially the pyramidality of these atoms [the sums of valence angles are 355.6 and 347.3° respectively] are probably caused by the steric hindrance between the C(21) and C(31) methyl groups [their out of the N(21)–C(22)–C(32)–N(31) plane distances are 0.549(6) and −0.964(7) Å respectively].

The orientation of the molecule in the crystal lattice, in line with the space group symmetry, causes no superimposition of the molecules and therefore the molecular structure results in a network of intermolecular interactions where shortest contacts are between neighbouring molecules rather than molecules in the same column [N(11)$\cdots$N(11)^{i} 3.966(5), N(11)$\cdots$N(11)^{ii} 4.149(5), N(31)$\cdots$N(31)^{iii} 4.147(5), N(31)$\cdots$N(31)^{iv} 4.147(5) Å; $i = 3/2 - x, -1/2 - y, 1 - z$; $ii = 3/2 - x, 1/2 - y, 1 - z$; $iii = 3/2 - x, -1/2 + y, 3/2 - z$; $iv = 3/2 - x, 1/2 + y, 3/2 - z$]. The other intermolecular contacts are consistent with van der Waals interactions.

Conclusions

The reaction of indole with nitrosobenzene in the presence of carboxylic acids mainly affords a mixture of the radical cation **8** and the dication **9**, which are formed by oxidation of the trimer indole **7**. Because the mixture **8**–**9** shows electrochemical conductivity it was important to elucidate the structure of the two compounds and their ratio, in order to understand which of the two species is determinant for the electrical conductivity.

The few results[2] concerning the electrical conductivity are in agreement with those of other conducting organic compounds such as polymers obtained from a variety of monomers which include thiophene,[9–12] furan,[13] carbazole,[14,6] thionaphthene-indoles[15] and pyrroles.[16]

Our results have prompted us to start a study to explain the role of the two species, radical cation–dication, in electrical conductivity.

Experimental

Melting points were measured with an Electrothermal apparatus and are uncorrected. 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 on a Gemini Varian 200 MHz spectrometer. EPR 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*-factors, which were corrected with respect to that of the radical cation of perylene in conc. sulfuric acid. Mass spectra were recorded in EI$^+$ mode on a Carlo Erba QMD 1000 GC-MS spectrometer equipped with a direct probe apparatus. UV spectra were recorded on a Uvikon 941 spectrophotometer. HPLC measurements were carried out on a Hewlett Packard series 1000 at 25 °C using a C-18RP column and MeCN–H$_2$O (9 : 1) as eluant.

Indole, nitrosobenzene, acetic acid, monochloro-, monobromo- and trichloro-acetic acid, phenylhydrazine, potassium *tert*-butoxide and DMSO were Aldrich commercial products and used without further purification. Compound **11** was prepared as previously described starting from pure **7**.[1] Crystals suitable for X-ray analysis were obtained by evaporating a solution of **11** in ethyl acetate.

Reaction of indole 1 and nitrosobenzene 2 in the presence of acid. General procedure

Nitrosobenzene (1.07 g, 10 mmol in 10 ml of CH$_2$Cl$_2$) was added dropwise under stirring to a solution of a mixture of indole (1.17 g, 10 mmol) and the appropriate acid (10 mmol) in 10 ml of CH$_2$Cl$_2$ under nitrogen at room temperature. The colour of the solution changed rapidly from green to green–yellow and then to dark violet with monochloro-, monobromo- and trichloro-acetic acid. Slower colour changes were observed for the reaction catalysed with acetic acid. All reactions were kept for 12 h before working up. The deep-green precipitate was filtered off (see below for each reaction) and the filtrate was washed with 5% aqueous NaHCO$_3$ (3 × 20 ml). The organic layer was separated, dried over Na_2SO_4 and evaporated to dryness. From the residue compounds **3**–**7** were separated and identified as previously described,[1] their yields being similar to those already reported.[1]

Characterisation of the deep-green precipitate (mixture of 8 and 9) for each reaction

Reaction with acetic acid. Yield = 22.9%; mp = 153–156 °C; IR (KBr), ν, cm^{-1}: 3056, 1604, 1566, 1295, 1182, 1111, 742. **8a** : **9a** ratio determined by HPLC as 63 : 37. Analysis. Calcd. for $C_{26}H_{18}N_3O_2$ (63%), $C_{28}H_{22}N_3O_4$ (37%): C, 75.43; H, 4.59; N, 9.89. Found: C, 75.78; H, 4.61; N, 9.68%.

Reaction with monochloroacetic acid. Yield = 23.7%; mp = 170–172 °C; IR (KBr), ν, cm^{-1}: 3220, 3180, 3162, 3064, 1677, 1602, 1288, 1213, 1178, 1112, 740. **8b** : **9b** ratio determined by HPLC as 60 : 40. Analysis. Calcd. for $C_{26}H_{17}ClO_2$ (40%), $C_{28}H_{20}N_3Cl_2O_4$ (60%): C, 65.29; H, 3.83; N, 8.08. Found: C, 65.33; H, 3.78; N, 7.86%.

Reaction with monobromoacetic acid. Yield = 21.3%; mp = 208–210 °C; IR (KBr), ν, cm^{-1}: 3263, 3170, 3143, 3056, 1691, 1612, 1290, 1203, 1180, 1111, 738. **8d** : **9d** ratio determined by HPLC as 33 : 67. Analysis. Calcd. for $C_{26}H_{17}N_3BrO_2$ (33%), $C_{28}H_{20}N_3Br_2O_4$ (67%): C, 57.54; H, 3.34; N, 7.39. Found: C, 57.67; H, 3.27; N, 6.97%.

Reaction with trichloroacetic acid. Yield = 51.6%; mp = 240–243 °C; IR (KBr), ν, cm^{-1}: 3284, 3264, 3052, 1745, 1678, 1326, 1211, 1101, 737. **8c** : **9c** ratio determined by HPLC as 47 : 53. In this case the elemental analysis is not in good agreement with the ratio determined by HPLC.

HPLC Measurements. General procedure

The green precipitate containing **8** and **9** (0.7 mg) was dissolved in DMSO (1 ml) and CH_3CN (10 ml) and treated with 4-aminopyridine (10 mg) under stirring. After 1 h the solution was quantitatively transferred into a volumetric flask and CH_3CN was added up to 20 ml. The **8** : **9** ratio was established by comparing the ratio of the areas of the peaks of **7** and **10** obtained by treating the mixture with 4-aminopyridine with the ratio of the areas obtained with a solution containing compounds **7** and **9** in 1 : 1 ratio. The UV detector was set at 278 nm.

Synthesis of compound 7 from the mixture of 8 and 9

A solution of phenylhydrazine (350 mg in 5 ml of CH_3CN) was added dropwise under stirring at room temperature to a suspension of **8b** and **9b** (1.2 g) in CH_3CN (25 ml). The solution became colourless with time and a white precipitate formed. After 2 h the precipitate was filtered off under vacuum and washed with 5 ml of cold CH_3CN: 890 mg (yield = 93%) of **7** were isolated; mp = 338 °C from CH_3CN (lit. 300–304 °C);[12,14] UV, λ_{max} = 345, 302 and 251 nm in $CHCl_3$; IR (KBr), ν, cm^{-1}: 3407, 3324, 3267, 3049, 1641, 1614, 1327, 1249, 1176, 760. ^{1}H-NMR, δ (d_6-DMSO): 7.40 (m, 6H, arom), 7.78 (m, 3H, arom), 8.79 (m, 3H, arom), 11.31 (s, 1H, NH), 11.41 (s, 1H, NH), 11.84 (s, 1H, NH) ppm. M_r for $C_{24}H_{15}N_3$, 345.39; MS (EI$^+$): m/z = 346 (6%), 345 (100), 344 (34), 172 (48), 171 (12).

Synthesis of compound 10 by oxidation of 7

Lead dioxide (1.5 g) was added to a solution of **7** (343 mg, 1 mmol in 100 ml of benzene) and the mixture was heated at 75 °C under stirring for 2 h. The reaction mixture was cooled to room temperature and the product was filtered off along with the lead salts. The filtered material was extracted with 15 ml of boiling DMF. By cooling the DMF solution compound **10** precipitated in nice brown needles: 205 mg (yield = 60%); mp > 350 °C from DMF; UV, λ_{max} = 448 and 278 nm from $CHCl_3$; IR (KBr), ν, cm^{-1}: 3056, 1646, 1540, 1299, 1099, 748. ^{1}H-NMR, δ (d_6-DMSO): 6.91 (m, 1H, arom), 7.20 (m, 7H, arom), 7.56 (d, 1H, J = 7.34 Hz), 7.64 (d, 1H, J = 7.34 Hz), 7.75 (d, 1H, J = 7.70 Hz), 7.96 (s, 1H, arom), 12.34 (s, 1H, NH) ppm. M_r for $C_{24}H_{13}N_3$, 345.39; MS (EI$^+$): m/z = 346 (25%), 345 (100), 344 (9), 173 (13), 172 (22), 171 (8).

Reduction of 10 to 7 by phenylhydrazine

A suspension of compound **10** (115 mg, 0.3 mmol) in CH_3CN (10 ml) was treated with phenylhydrazine (36 mg, 0.3 mmol in 2 ml of CH_3CN) under stirring at room temperature. In time the solution became colourless and a white precipitate appeared, which, after 2 h, was filtered off under vacuum: 82 mg (yield = 71%) of **7** were isolated. The reaction must be considered quantitative because the filtrate contained only compound **7** as verified by TLC.

Oxidation of 7 with nitrosobenzene in the presence of monochloroacetic acid

A solution of nitrosobenzene (34 mg, 0.32 mmol in 5 ml of CH_2Cl_2) was added, at room temperature and under stirring, to a solution of **7** (50 mg, 0.15 mmol) in 15 ml of CH_2Cl_2. The solution turned suddenly to a deep-green colour and a precipitate appeared. After 1 h, the precipitate (46.3 mg), which was a mixture of **8** and **9**, was filtered off. In this case the ratio **8** : **9** was not determined.

Oxidation of 7 with iodine

A solution of iodine (19 mg, 0.075 mmol in 10 ml of CH_2Cl_2) was added, at room temperature and under stirring, to a solution of **7** (50 mg, 0.15 mmol) in 20 ml of CH_2Cl_2. After 7 h the green precipitate, a mixture of **8e** and **9e** in 1 : 1 ratio (55 mg, mp = 305 °C), was filtered off and washed with 10 ml of CH_2Cl_2. Analysis. Calcd. for $C_{24}H_{15}N_3I$ (50%), $C_{24}H_{15}N_3I_2$ (50%): C, 54.60; H, 2.86; N, 7.90. Found: C, 54.52; H, 2.56; N, 7.83%.

Radical cation 8b by comproportionation of 7 and 10 in the presence of monochloroacetic acid

Monochloroacetic acid (40 mg, 0.42 mmol) in CH_2Cl_2 (10 ml) was added at room temperature and under stirring to a solution of **7** (35 mg, 0.1 mmol) and **10** (35 mg, 0.1 mmol) in CH_2Cl_2 (25 ml). The starting brown solution became green and a precipitate was obtained. After 6 h the precipitate was filtered off (the filtrate was almost colourless) and washed under stirring with 10 ml of benzene for 2 h. The solid was filtered and washed with dried ethyl ether: 72 mg of **8b** were obtained. Yield = 80%, mp = 188–190 °C (decomp.). Analysis. Calcd. for $C_{26}H_{17}N_3ClO_2$: C, 71.15; H, 3.90; N, 9.57. Found: C, 70.91; H, 3.89; N, 9.68%.

Synthesis of 12 by treatment of 10 with monochloroacetic acid

Compound **10** (35 mg, 0.1 mmol) in CH_2Cl_2 (20 ml) was treated, under stirring at room temperature, with a solution of monochloroacetic acid (95 mg, 1 mmol). After 4 h the brown precipitate was filtered off and washed with benzene: obtained 41 mg of **12**. Yield = 92%; mp = 225–230 °C (decomp.). IR (KBr), ν, cm^{-1}: 3218, 3185, 3086, 2956, 1855, 1691, 1544, 1228, 1153, 754. Analysis. Calcd. for $C_{26}H_{16}N_3ClO_2$: C, 71.31; H, 3.68; N, 9.59. Found: C, 71.17; H, 3.58; N, 9.45%.

EPR Measurements

(A) EPR of the deep-green precipitate. The precipitates obtained in the main reaction were powdered with KBr (5% of precipitate). The powders were put in thin capillary tubes situated inside the EPR cavity: in each case a very intense signal was recorded.

Table 3 Experimental data for the X-ray diffraction studies on crystalline compound **11**

Formula	$C_{27}H_{21}N_3$
Fw	387.4
Crystal system	Monoclinic
Space group	*C*2/*c*
Cell parameters at 298 K	
a/Å	22.465(4)
b/Å	8.017(2)
c/Å	21.376(4)
α/deg	90
β/deg	100.1(1)
γ/deg	90
V/Å^3	3790.2(20)
Z	8
D_c/g cm^{-3}	1.36
Crystal dimens./mm	0.23 × 0.23 × 0.33
Linear abs. coeff./cm^{-1}	6.2
Unique total data	7304
Criterion of obsn.	$I > 2\sigma(I)$
Unique obs. data (NO)	1567
No. of refined par. (NV)	271
Overdetermn. ratio (NO/NV)	5.8
R[b]	0.049
R_w[c]	0.054
GOF[d]	3.5
Largest shift/esd	0.6
Largest peak/e Å^{-3}	0.14
Programs	[a]

[a] SHELXS86,[17] SHELX76,[18] PARST.[19] [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] $\text{GOF} = [\Sigma w|\Delta F|^2/(\text{NO} - \text{NV})]^{1/2}$.

(B) Radical cation 8f. Compound **7** was dissolved in concentrated sulfuric acid. The resulting green solution was put in an EPR aqueous cell situated inside the spectrometer cavity: a very intense and unresolved signal was recorded.

(C) Radical anion of compound 10. Reaction of compound **10** with Bu^{t}OK in DMSO led to the detection of a very intense signal of the corresponding radical anion.

Electrochemical measurements

Voltammetric measurements were performed with a three-electrode multipolarograph (AMEL 472/WR) coupled with a digital *x*/*y* recorder (AMEL 863), using a glassy-carbon (GC) electrode as working, Hg–Hg_2Cl_2–NaCl (sat. aq.)–DMF–Et_4NClO_4-sintered glass disk[20] as reference and a platinum wire as counter electrode. All experiments were carried out at room temperature in nitrogen-purged solution of anhydrous DMF (Aldrich) containing 0.1 mol L^{-1} Bu$^t_4$NBF$_4$ (Carlo Erba) as supporting electrolyte and 5.0 × 10^{-4} mol L^{-1} substrate. Acids of different strength, from xylenol to trichloroacetic acid, were used as protonating agents.

Spectroelectrochemical studies were carried out with a diode array spectrophotometer HP 8452A, a potentiostat (AMEL 552) coupled with an integrator (AMEL 731) and an *x*/*y* recorder (LINSEIS L250E), using a UV three-electrode modified cell, a platinum wire as working electrode, an Ag/$AgClO_4$ (0.1 mol L^{-1})–MeCN/fine-porosity fritted glass-disk/DMF–Et_4NClO_4-sintered glass disk as reference and a platinum wire (placed in the inner wall of a glass tube and connected to the test solution *via* a sintered glass-disk) as counter electrode. UV–VIS spectra of compounds **7**, **10** and **11** (~5 × 10^{-4} mol L^{-1}) were recorded in anhydrous DMF containing Bu$^t_4$NBF$_4$ (0.1 mol L^{-1}). Compound **10** (5.0 × 10^{-4} mol L^{-1}) was electrolysed in the UV cavity in the presence of xylenol in the ratio 10 : 1.

Crystal structure of 1,2,7-trimethyl-2,7-dihydro-1*H*-diindolo-[2,3-*a*:2,3-*c*]carbazole, 11

Table 3 shows the experimental and crystallographic data for **11**. The intensities I_{hkl} were determined at room temperature by analysing the reflection profiles by the Lehmann and Larsen procedure.[21] One standard reflection measured every 100 collected reflections to monitor crystal decomposition and instrumental linearity showed no significant variations. Corrections for Lorentz and polarisation effects were performed; there were no corrections for absorption effects. The structures were solved by direct methods and refined by cycles of full-matrix anisotropic least-squares; the hydrogen atoms were located in the difference map and included in the final structure factors calculation as fixed contributors.

Atomic scattering factors were from the International Tables for X-Ray Crystallography.[22] Bibliographic searches were carried out using the Cambridge Structural Database Files through the Servizio Italiano di Diffusione Dati Cristallografici, Parma, Italy.

CCDC reference number 188/270. See http://www.rsc.org/suppdata/p2/b0/b001609h/ for crystallographic files in .cif format.

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