

Radical Cations. Chemical and Electrochemical Oxidative Dimerization of 1,2-Dihydro-2,2-disubstituted-3-oxo-3H-indoles (Indoxyls) and Some C-5 and C-7 Monosubstituted and Disubstituted Derivatives

Corrado Berti,[†] Lucedio Greci,^{*†} Romano Andruzzi,[‡] and Antonio Trazza^{*†}

Istituto Chimico della Facoltà di Ingegneria della Università, Viale Risorgimento, 2-40136 Bologna, Italy, and Dipartimento di Ingegneria Chimica, Università "La Sapienza", and Centro di Studio per la Elettrochimica e la Chimica Fisica delle Interfasi del C.N.R., Via del Castro Laurenziano, 7-00161 Roma, Italy

Received April 24, 1984

Chemical and electrochemical oxidation of indoxyls has been investigated in MeCN. The mechanism, which involves coupling of the primary oxidation product (monomer radical cation) to form a dimer radical compound, is electrochemically described by an ECE process. Dimers are oxidized in two reversible, one-electron steps at potentials less positive than those required for oxidation of the parent compound. Both chemical and electrochemical results show that dimerization occurs through a C-C, C-N, or N-N bond, depending on the substituents on the nitrogen of the indoxyl nucleus ring. Both oxidation techniques produced relatively stable radical cations; their ESR signals were recorded. Monomer radical cations were obtained only for indoxyl 1m and indoline 1l. The synthesis of some dimers by metal ion oxidation of the corresponding monomer allowed the structure assignment of the C-C dimer radical cations; for other radicals the structure was determined on the basis of ESR data. The reactivity of monomer and dimer radical cation is explained on the basis of the combined chemical and electrochemical results.

1,2-Dihydro-2,2-disubstituted-3-oxo-3H-indoles (indoxyls) contain a carbonyl and an amine group and can be considered suitable systems for generating radical anions and radical cations by reduction and oxidation, respectively. Previously we studied the stereochemical reduction of the carbonyl group both by chemical¹ and electrochemical means.^{1,2} In the present paper we describe the chemical and electrochemical oxidation of these compounds, the reactivities of the one-electron oxidation products, i.e., monomer radical cations, and the behavior of the dimer radical cations. This study was suggested by the current interest in radical cations, which play an increasingly important role in oxidative electron transfer³ and display high, complex reactivity.⁴

Results

(A) Chemical Oxidation. The oxidation of indoxyls 1a-m (the numbered structures are given in Scheme I-III) in MeCN at room temperature in the ESR cavity allowed us in general to detect a well resolved signal. It was attributed to the monomer radical cation for indoxyl 1m (Table I). No signal was detected for 1f; signals in other cases (1a-e, 1g-l) corresponded to different dimer radical cations. There follows a description of the individual cases.

Indoxyls 1a-e and 1j-l, oxidized with I₂/AgClO₄, formed the corresponding dimer radical cations 3⁺ (Scheme I). The C-C dimerization mainly occurred at C-5 of the benzene ring of the indoxyl nucleus. This is in agreement with the spin density distribution calculated for the monomer radical cation 2⁺ (Table II). The NMR spectrum of dimer 4 (see Experimental Section)⁵ confirms the structure attributed to 4 and the C-C dimerization at C-5. Furthermore, the ESR spectrum obtained by oxidation of 4 with I₂/AgClO₄ was identical with that obtained for the oxidation of the monomer 1k. The oxidation of 1h, C-5 *tert*-butoxy substituted, gave the dimer radical cation 3h⁺ involving C-7 (Figure 1). The hyperfine coupling constants (h.f.c.cs) agree with a dimeric structure (Table I).

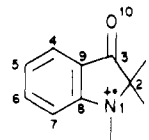
Indoxyl 1g, which is *tert*-butoxy substituted at C-7, gave radical cation 7⁺ through a N-C dimerization (Scheme IIIa). The structure of radical cation 7⁺ was deduced from

Table I. Hyperfine Coupling Constants in Gauss for MeCN Solution of Radical Cations 2m⁺, 3a-e⁺, 3h⁺, 3j-l⁺, 7⁺, 12⁺, and 13⁺^a

| | $a^{\text{H-NH}}$ or $a^{\text{H-NMe}}$ | $a^{\text{H-4}} =$ $a^{\text{H-6}}$ | $a^{\text{H-5}}$ | $a^{\text{H-7}}$ | a^{N} |
|-----------------|--|--|---------------------------------|------------------|----------------|
| 2m ⁺ | 5.80 (3H) | 0.50 (2H) | | 2.37 (1H) | 4.82 (1N) |
| 3a ⁺ | 4.00 (2H) | 0.40 (4H) | | 1.62 (2H) | 4.00 (2N) |
| 3b ⁺ | 4.00 (2H) | 0.40 (4H) | | 1.62 (2H) | 4.00 (2N) |
| 3c ⁺ | 3.74 (2H) | 0.45 (4H) | | 1.40 (2H) | 3.74 (2N) |
| 3d ⁺ | 3.98 (2H) | 0.45 (4H) | | 1.53 (2H) | 3.93 (2N) |
| 3e ⁺ | 3.90 (2H) | 0.45 (4H) | | 1.60 (2H) | 3.93 (2N) |
| 3h ⁺ | 3.55 (2H) | 0.32 (4H) | | | 3.60 (2N) |
| 3j ⁺ | 5.00 (6H) | | | 1.00 (2H) | 4.75 (2N) |
| 3k ⁺ | 4.57 (6H) | 0.37 (4H) | | 1.28 (2H) | 4.57 (2N) |
| 3l ⁺ | 4.82 (6H) | | | 1.25 (2H) | 4.62 (2N) |
| 7 ⁺ | 6.75 (1H) | | $a^{\text{Nexo}} = 6.0$ (1N) | | 6.37 (1N) |
| 12 ⁺ | 8.25 (1H) | | | | 7.75 (1N) |
| 13 ⁺ | | 0.55 (2H) | | 2.25 (2H) | 5.85 (2N) |

^a All spectra were recorded at room temperature.

Table II. Spin Density Distributions



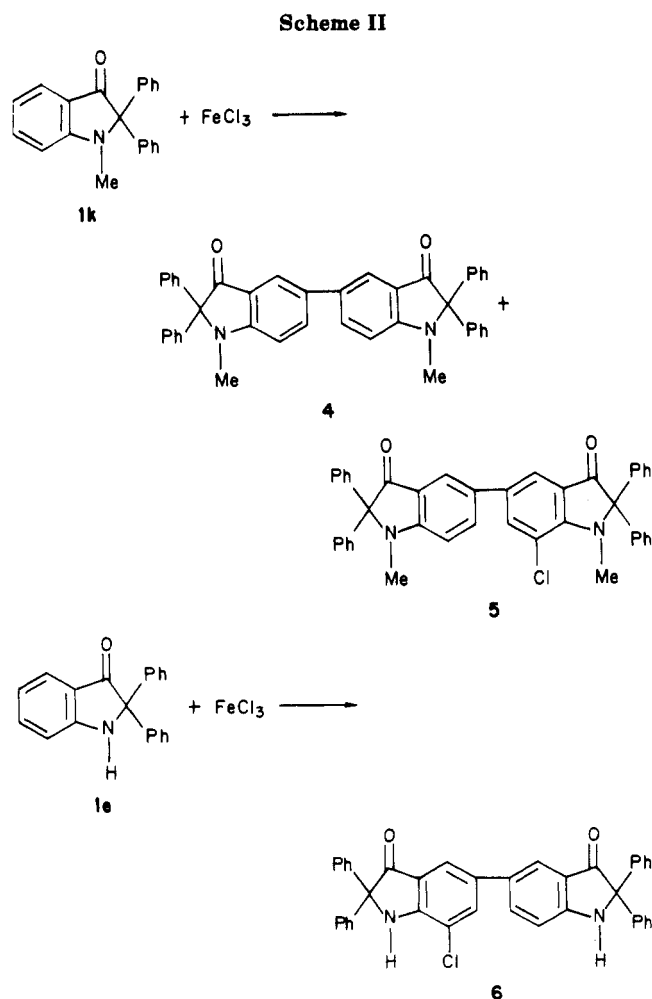
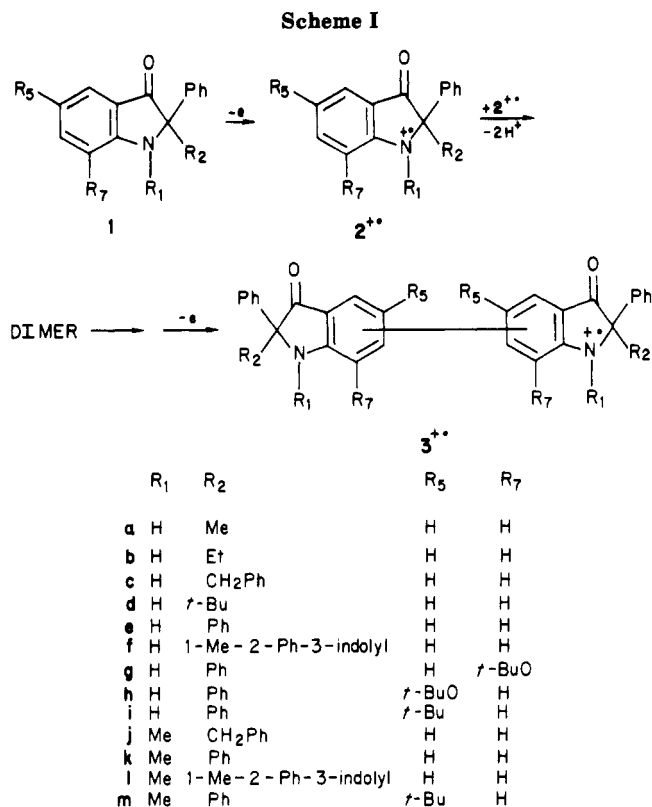
| position | McLachlan spin density |
|----------|------------------------|
| 1 | 0.2777 |
| 3 | -0.0014 |
| 4 | 0.0302 |
| 5 | 0.2789 |
| 6 | -0.0778 |
| 7 | 0.2460 |
| 8 | 0.1287 |
| 9 | 0.0999 |
| 10 | 0.0179 |

its h.f.c.cs (Table I), which do not agree with those of the C-C dimers. This result is supported by other experi-

(1) Berti, C.; Greci, L.; Poloni, M. *J. Chem. Soc., Perkin Trans. 2* 1980, 710.

(2) (a) Andruzzi, R.; Trazza, A.; Greci, L.; Marchetti, L. *Ann. Chim. (Rome)* 1979, 69, 583. (b) Berti, C.; Greci, L.; Marchetti, L.; Andruzzi, R.; Trazza, A. *J. Chem. Res. Synop.* 1981, 340; *J. Chem. Res. Miniprint* 1981, 3944.

[†] Istituto Chimico della Facoltà di Ingegneria della Università.
[‡] Università "La Sapienza".



mental evidence observed in the oxidation of carbazole derivatives.^{6a-c}

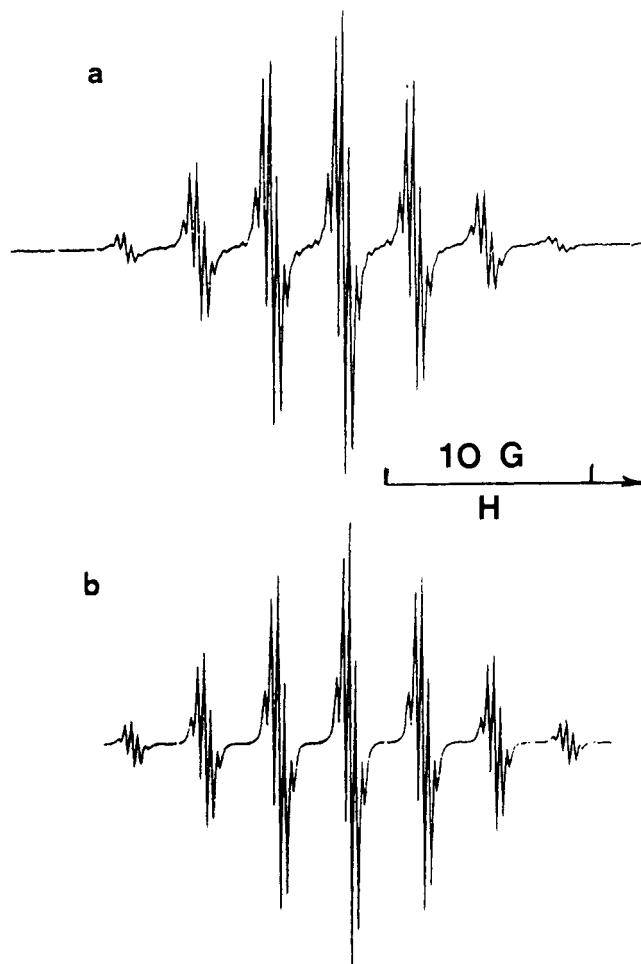


Figure 1. ESR spectrum of $3h^+$ recorded at room temperature: (a) experimental; (b) computer simulated with a line width of 0.13 G.

Indoxyl **1f**, which bears an indolyl group at C-2 and a hydrogen at the nitrogen, did not give the corresponding radical cation $3f^+$, but it led to 2-phenyl-3H-indol-3-one (**9**) and indole **10** (Scheme IIIb).⁷ To have further information about C-5 and C-7 mono- and disubstituted indoxyls we also studied compounds **11**, **1i**, and **1m** (see experimental). Oxidation of indoline **11** in MeCN gave the expected monomer radical cation 12^+ (Scheme IIIc).⁸ Oxidation of **1m** formed the corresponding monomer radical cation $2m^+$ (Figure 2), whereas the oxidation of

(3) Ebersson, L.; Jönsson, L.; Wistrand, L.-G. *Tetrahedron* **1982**, *38*, 1087.

(4) Bard, A. J.; Ledwith, A.; Shine, H. J. *Adv. Phys. Org. Chem.* **1976**, *13*, 155.

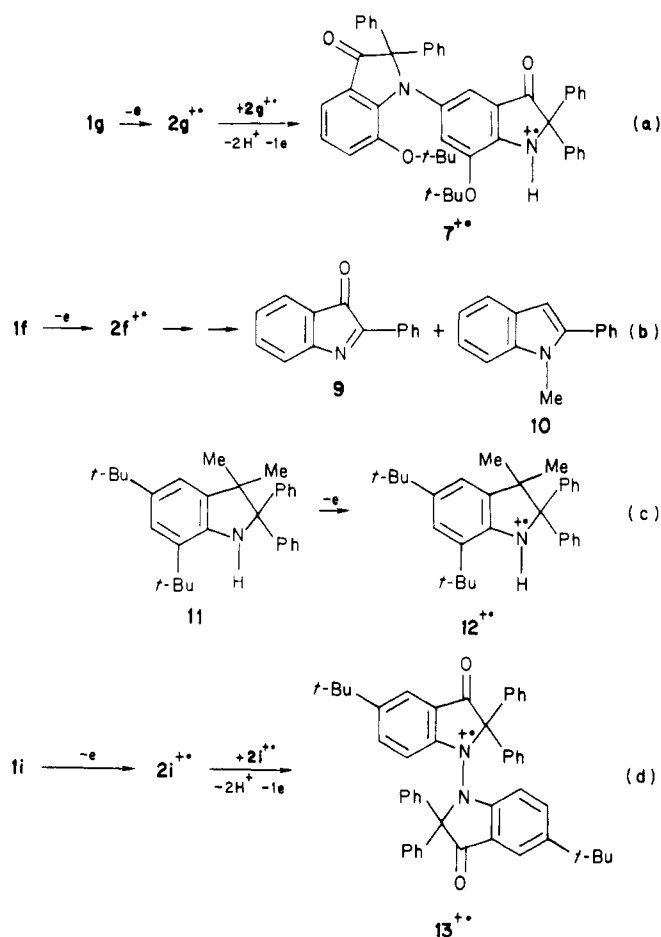
(5) The multiplicity of these signals has already been observed for C-5 substituted indoxyls and differs from that of C-7 substituted indoxyls: Greci, L. *Tetrahedron* **1982**, *38*, 2435.

(6) (a) Hanson, P. "Advances in Heterocyclic Chemistry"; Katritzky, A. R., Boulton, A. J., Eds.; 1979; Vol. 25, p 205. (b) Ambrose, J. F.; Nelson, R. F. *J. Electrochem. Soc.* **1968**, *115*, 159. (c) Ambrose, J. F.; Carpenter, L. L.; Nelson, R. F. *Ibid.* **1975**, *122*, 876. (d) Cauquis, G.; Cognard, J.; Serve, D. *Tetrahedron* **1971**, *27*, 4645.

(7) The behavior of **1f** can probably be explained assuming that radical cation 7^+ , formed in the first oxidation step, undergoes a retrogression reaction owing to the high leaving power of the indolyl group at C-2 and assisted by the NH group; in fact, the corresponding *N*-methyl substituted 21^+ follows the normal C-C dimerization at C-5. Retrogression reactions were observed in similar derivatives: Colonna, M.; Greci, L.; Marchetti, L. *Gazz. Chim. Ital.* **1975**, *105*, 985.

(8) The high h.f.c.s values ($a^N = 7.75$ G and $a^{H-NH} = 8.25$ G) obtained for radical cation 12^+ can in our opinion be attributed to the absence of the carbonyl group at C-3 and to the steric hindrance of the *tert*-butyl group at C-7, which increases the spin density on the nitrogen atom by compromising the coplanarity of the NH group and the benzene ring of the indoxyl nucleus.

Scheme III



1i gave the dimer radical cation 13^{++} (Figure 3), through the only example observed of N-N dimerization (Scheme III d). The structure of radical cation 13^{++} was proposed on the basis of its h.f.c.s which are quite different from those of C-C and C-N dimer radical cations $3a-h^{++}$ and 7^{++} (Table I). The N-N dimerization is not surprising, as it also occurs in carbazole systems,^{6a-c} and it is the only process observed in the oxidation of diphenylamine under particular conditions.^{6d}

Dimers 4, 5, and 6 were obtained by oxidizing 1k and 1e with Fe(III) in MeCN at room temperature. Indoxyls 1i and 1m were prepared by reacting 1e and 1k, respectively, with *tert*-butyl chloride and $AlCl_3$. The structures of these compounds were determined on the basis of their analytical and spectroscopic data (see Experimental Section).

(B) Electrochemical Oxidation. In the concentration range 10^{-4} – 10^{-2} M and at a potential span up to 1.5–1.6 V (vs. Ag/Ag^+) indoxyls 1a–m examined in MeCN with Et_4NClO_4 as supporting electrolyte at a pulsed platinum electrode (ppe) exhibited a well defined oxidation step. A second step occurred in some cases; however it appears so near to the background process that it could not be characterized. Voltammetric data for indoxyls 1a–m are reported in Table III and a typical voltamperogram (1m) is shown in Figure 4 (curve A). 5,5'-Biindoxyl 4 and indoline 11 are also included in the same Table to compare the behavior of the studied compounds both with that of a related dimeric species 4 and with that of a stable radical cation 12^{++} . From the data reported in Table III it appears that dimer 4 is oxidized in two successive steps, both of which occur at potential less anodic than the step of the indoxyl parent 1k. Moreover, comparing the function i/c for indoxyls 1a–m with the corresponding values calculated

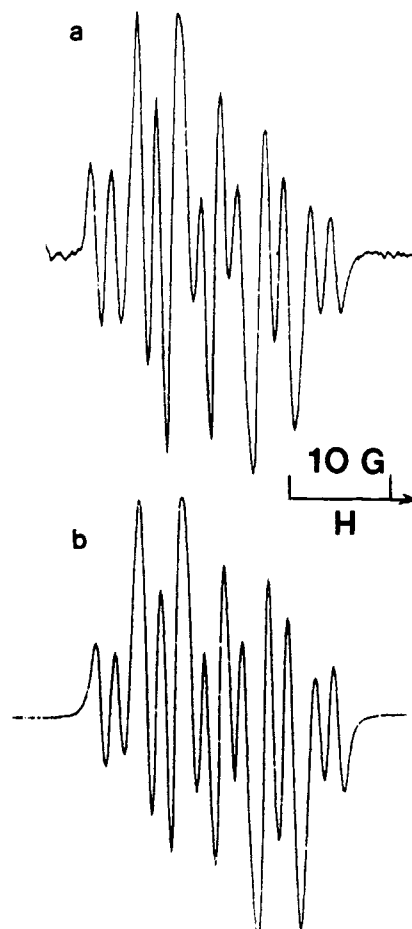


Figure 2. ESR spectrum of $2m^{++}$ recorded at room temperature: (a) experimental; (b) computer simulated with a line width of 0.30 G.

Table III. Voltammetric Data for the Oxidation of Indoxyls 1a–m, Indoline 11, and Dimer 4 in MeCN at a Platinum Electrode^a

| no. | first step | | |
|-----------------|---------------|-----------------|--------------------------|
| | $E_{1/2}$, V | i_1 , μA | i_1/c , μAmM^{-1} |
| 1a | 0.91 | 3.80 | 3.45 |
| 1b | 0.87 | 3.82 | 3.54 |
| 1c | 0.88 | 3.76 | 3.51 |
| 1d | 0.86 | 4.30 | 3.80 |
| 1e | 0.93 | 3.80 | 3.45 |
| 1f ^b | 0.75 | 3.52 | 3.74 |
| 1g ^b | 0.69 | 2.60 | 1.85 |
| 1h | 0.78 | 2.72 | 2.77 |
| 1i | 0.89 | 2.94 | 2.82 |
| 1j | 0.80 | 4.32 | 2.88 |
| 1k | 0.81 | 4.00 | 3.67 |
| 11 ^b | 0.68 | 3.76 | 2.90 |
| 1m | 0.81 | 2.08 | 2.06 |
| 4 ^c | 0.52 | 0.84 | 1.60 |
| 11 | 0.42 | 2.08 | 2.00 |

^a Solutions containing about 1×10^{-3} M indoxyl in MeCN–0.1 M Et_4NClO_4 ; the potentials are referred to $Ag/AgClO_4$ 0.1 M in MeCN solution. ^b The second step showed an ill defined curve at ca. 1.2 V for 1f and at ca. 1.1 V for 1g and 1i. ^c The second step is characterized by $E_{1/2} = 0.74$ V and $i_1 = 0.84 \mu A$.

for indoline 11 and the reversible one-electron oxidation process of 2,2-disubstituted 3-oxoindolin-1-oxyls⁹ under the same experimental conditions one concludes that the number of electrons (n) involved is $1 < n < 2$ for indoxyls 1a–i and 1h–l and $n = 1$ for 1g and 1m. It is worth noting

(9) Andruzzi, R.; Trazza, A.; Berti, C.; Greci, L. *J. Chem. Res. Synop.* 1982, 178; *J. Chem. Res. Miniprint* 1982, 1840.

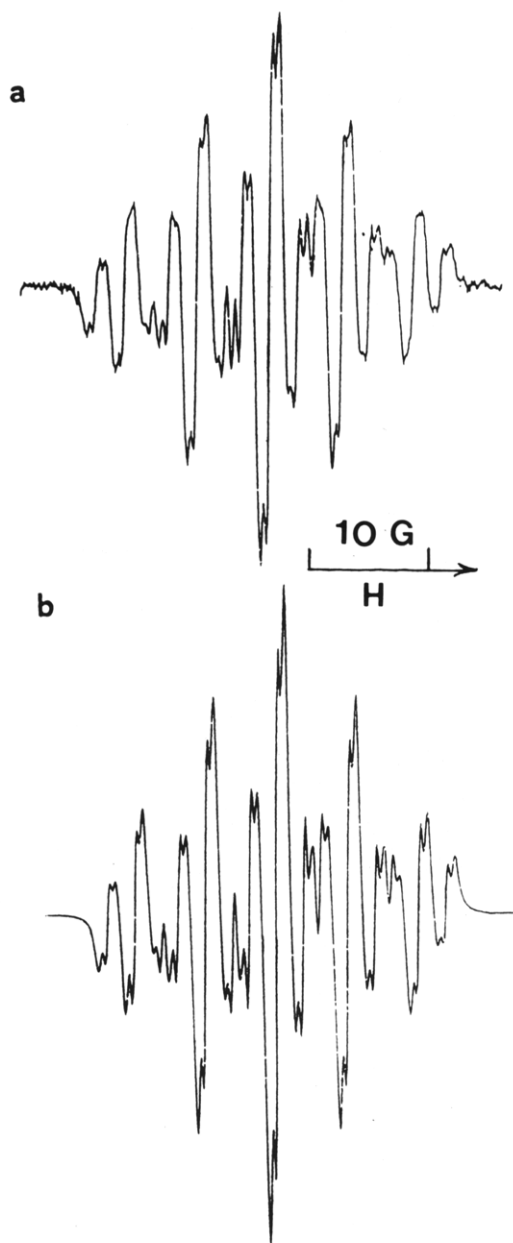


Figure 3. ESR spectrum of $12^{+\bullet}$ recorded at room temperature: (a) experimental; (b) computer simulated with a line width of 0.18 G.

that both electron-transfer steps of the dimer **4** represent a one-electron oxidation process. For indoxyls **1a–f** and **1h–l** the oxidation process appears to involve a very rapid reaction of the primary one-electron product to form species which are further oxidized at the same potential as the parent compound. Therefore, to test the stability of the one-electron oxidation product as well as to compare the electrochemical data with those from chemical oxidation (Section A), the behavior of indoxyls **1a–m** was examined by cyclic voltammetry, controlled-potential coulometry, and ESR spectroscopy. The following behaviors were observed.

Indoxyls 1g and 1m. In the voltage excursions from zero toward positive potentials up to 1.2 V, indoxyls **1g** and **1m** showed at a stationary platinum electrode (spe) anodic peaks (I_a , with $E_{pa} = 0.71$ and 0.85 V at 0.2 V s^{-1} for **1g** and **1m**, respectively), which correspond to the oxidation step observed at the ppe. Reversal of the scan revealed the complementary cathodic peaks (I_c , with $E_{pc} = 0.64$ and 0.78 V, for **1g** and **1m**, respectively) due to the reduction

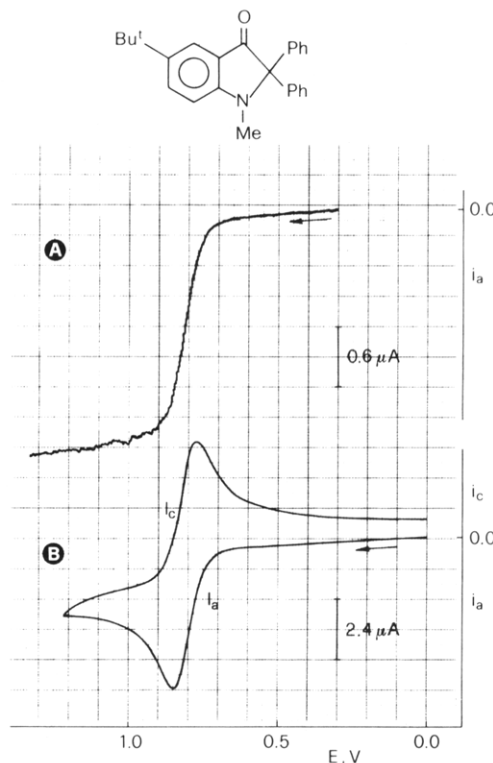


Figure 4. DC (curve A) and cyclic (curve B) voltamperograms of 1.01 mM indoxyl **1m** in MeCN–0.1 M Et_4NClO_4 . (Scan rate 0.2 V s^{-1} .)

of the primary oxidation product. A typical voltamperogram (indoxyl **1m**) is reported in Figure 4 (curve B). The parameters of this anodic–cathodic system meet the diagnostic criteria¹⁰ expected for a reversible one-electron process producing a species (radical cation, see below), which is stable even at scan rates as slow as 0.1 V s^{-1} . Controlled-potential electrolysis (at 1.0 V) confirms that the electrode process for **1m** involves one electron per molecule of reactant. Moreover, it also indicated that the primary oxidation product is stable during the time (8–15 min) of electrolysis. Portions of the resulting solution transferred into the ESR cavity gave a strong and stable signal which is identical with that recorded in the chemical oxidation (section A) and attributed to the radical cation $2m^{+\bullet}$. On the contrary, the oxidation at 0.78 V of indoxyl **1g** showed that the corresponding radical cation $2g^{+\bullet}$ is unstable during the time of the electrolysis. Nevertheless, if portions of the solution resulting after the release of about one electron per molecule of reactant are transferred into the ESR cavity, an intense signal is recorded. It was attributed to the radical cation of the C–N dimer $7^{+\bullet}$, which was also obtained in the chemical oxidation (section A, Scheme IIIa).

Indoxyls 1a–e and 1h–l. The cyclic voltammetric experiments showed that the corresponding one-electron oxidation product (radical cation $2a-e^{+\bullet}$ and $2h-l^{+\bullet}$) is quite unstable, even at scan rates as fast as 100 – 150 V s^{-1} . Only in the case of **1i** was a slight reversibility observed, i.e., a small complementary cathodic peak appeared at the fasted scan rates. On the other hand, for the corresponding *N*-methyl substituted indoxyl **1m** the reversibility was observed even at the lowest scan rates. Moreover, the oxidation had the characteristics of an electrochemical–chemical–electrochemical (ECE) mechanism, where each electrochemical step involves one electron per molecule of

(10) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

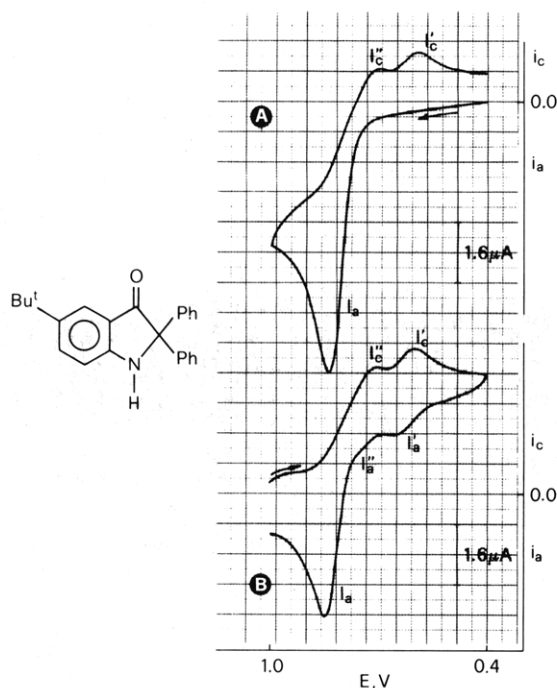


Figure 5. Cyclic voltamperograms of 1.05 mM indoxyl **1i** in MeCN–0.1 M Et₄NClO₄. (Scan rate 0.2 V s⁻¹.) Curve B was recorded holding the potential at 1.0 V for 20 s and then resuming the scan from 1.0 to 0.4 V.

reactant. Indeed, the current of the oxidation step of indoxyls **1a–e** and **1h–l** tends to be about twice that of indoxyls **1g** and **1m** (Table III). In addition, the cyclic voltamperograms recorded from 0.0 to 1.3 V did not show the complementary cathodic peaks (*I_c*), but rather two new cathodic peaks (*I_c'* and *I_c''*) in the region of 0.8–0.2 V, which can be attributed to the subsequent chemical reaction. It is worth noting that on both the successive scans from 0.0 to 1.3 V and on the first scan from 1.3 to 0.0 V, the two cathodic peaks (*I_c'* and *I_c''*) exhibit the corresponding anodic peaks (*I_a'* and *I_a''*), i.e., both *I_c'* and *I_c''* represent reversible processes. Two typical voltamperograms (indoxyl **1i** recorded with potential span from 0.4 to 1.0 V (curve A) and from 1.0 to 0.4 V (curve B)) are shown in Figure 5, and a typical voltamperogram (indoxyl **1k**, recorded with potential span from 0.0 to 1.15 V) is shown in Figure 6 (curve A). The same Figure 6 (curve B) also shows a voltamperogram of dimer **4** for comparison with the parent indoxyl **1k**. As can be seen (Figure 6, curve B) the dimeric species **4** exhibit two anodic peaks (*I_a'* and *I_a''*) with the corresponding cathodic peaks (*I_c'* and *I_c''*), which represent two reversible, one-electron processes. It is worth noting that the reduction peaks (*I_c'* and *I_c''*) of **4** are located at the same potentials as the cathodic peaks present in the voltamperogram of the parent indoxyl **1k** (see Figure 6 curves A and B). When the electrolysis of indoxyls **1a–e** and **1h–l**, carried out at a controlled-potential oxidation, was stopped after the release of about one electron per molecule of reactant and the resulting solution was transferred into the ESR cavity, an intense, stable signal was recorded. The ESR spectra obtained (Table I) were identical with those recorded in the chemical oxidation (see also section A).

Indoxyl 1f. As reported above the cyclic voltammetric behavior of indoxyl **1f** is somewhat different from that of the corresponding *N*-methyl derivative **1l**. In fact, the voltamperograms of **1f** recorded with a voltage excursion from 0.0 to 1.1 V showed an anodic peak (*I_a*) which corresponded to the oxidation step recorded at the ppe. The

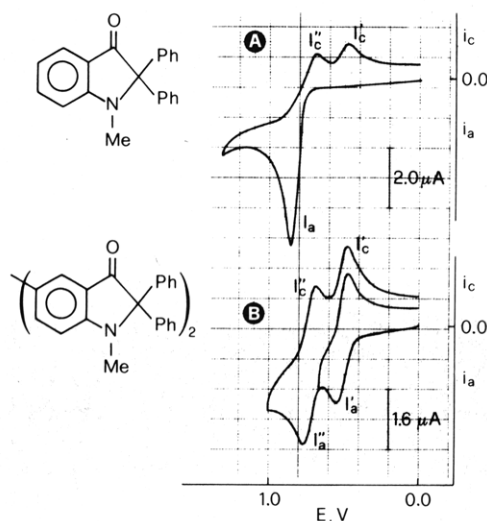
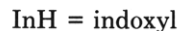
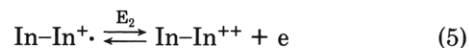
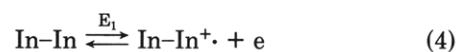
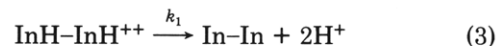
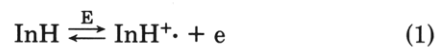


Figure 6. Cyclic voltamperograms of 0.99 mM indoxyl **1k** (curve A) and 0.08 mM 5,5-biindoxyl **4** (curve B) in MeCN–0.1 M Et₄NClO₄. (Scan rate 0.1 V s⁻¹.)

electrolysis at a controlled potential (0.9 V) tended to involve more than two electrons per molecule of **1f**, portions of the solution drawn from the cell during the electrolysis were magnetically inactive, and its TLC showed the presence of **9** and **10**.⁷

Discussion

On the basis of both chemical and electrochemical results we can conclude that the studied indoxyls in general undergo oxidative coupling to form a dimer radical cation as the final product. A behavior of this kind, which is very similar to that observed by others for the chemical¹¹ and electrochemical⁶ oxidation of carbazoles, can be explained by an ECE mechanism given in eq 1–5.



The cyclic voltammetric studies gave relevant information about the stability of the monomer radical cation. In fact, the dimerization rates of monomer radical cations **2a–e**⁺, **2h**⁺, and **2j–l**⁺ can be considered rather high,¹² as demonstrated by the absence of a reversible reduction peak accompanying the oxidation peak in the cyclic voltammetric experiments of indoxyls **1a–e**, **1h**, and **1j–l**. The cyclic voltammetry of indoxyl **1g** shows that the reduction peak is present also at rather low scan rates of the potential, and that the coupling of radical **2g**⁺ goes into effect in the time of the electrolysis. Finally, the coupling of radical **2m**⁺ does not occur even in a time longer than that of the electrolysis, so that we could record the signal corresponding to **2m**⁺. The positions at which one would expect for coupling of radical cations **2**⁺ are 1, 5, and 7

(11) Neugebauer, F. A.; Fischer, H.; Bamberger, S.; Smith, H. O. *Chem. Ber.* 1972, 105, 2694.

(12) The dimerization constant rate of carbazole radical cations was found to be on the order of 10⁷ M⁻¹ s⁻¹ (see ref 6c).

as shown in Table II. The experimental results point out that the coupling generally occurs at one of the above positions, depending on the substituents and their positions in the indoxyl nucleus. In particular we can observe that (i) C₅-C₅ coupling is preferred when indoxyls are 1-methyl substituted and unsubstituted in the ring, (ii) C₇-C₇ and N-N dimerizations take place when the monomer radical cation is C-5 *tert*-butoxy and C-5 *tert*-butyl substituted, respectively, and (iii) C-N coupling seems to be preferred for C-7 *tert*-butoxy substituted indoxyl. We think that the rate-determining step of the oxidation process for indoxyl is the loss of protons from the dihydro cation, eq 3, ($k_1 \ll k$). This assumption is confirmed by the number of electrons involved in the electrolysis: the stoichiometry of the oxidation (eq 1-5) requires two electrons per molecule of indoxyl, whereas this value was found experimentally to be in the 1-2 range (Table III). However, it tends to two when traces of a weak base, such as water, are added to the solution, i.e., when the current is about twice that used in the oxidation of indoxyl 1m.

The low yield of dimer 4 obtained in the chemical oxidative dimerization of indoxyl 1k is attributed to the low oxidation potential of 4, which is below that of the corresponding indoxyl 1k, as stated above. The formation of monochloro-substituted dimers 5 and 6 can be explained by an interaction of either the dimer radical cation or the dication with chloride ion. In our opinion the second possibility can be discarded because a reaction of this kind should have led to the formation of a dichloro-substituted dimer, which was never isolated. Thus, also on the basis of the literature,¹³ we consider the reaction of the dimer radical cation with chloride ion to be the process operating in the formation of compounds 5 and 6.

Experimental Section

Melting points are uncorrected. IR spectra were recorded on a 257 Perkin-Elmer spectrophotometer. ¹H NMR spectra were recorded on a Varian XL-100 spectrometer. Mass spectra were recorded on a Varian 112-S apparatus. ESR spectra were recorded on a Varian E-4 spectrometer. Compounds 1a-e,¹⁴ 1f,⁷ 1g,⁵ 1h,⁵ 1j,^{2b} 1k,^{2b} 1l,¹⁵ and 1l¹⁶ were prepared as described in the literature.

Synthesis of 1i and 1m. Indoxyl 1e (1 mmol) and AlCl₃ (1.1 mmol) were mixed in *tert*-butyl chloride (4 mL) and stirred at room temperature for 2 h. The reaction mixture was then poured into water (50 mL) and extracted with benzene (2 × 25 mL). The benzene layer was separated, dried on Na₂SO₄, and chromatographed on a column of silica gel eluted with petroleum ether/ethyl acetate 9.5:0.5. The third yellow eluate was 1i (60% yield). In the same way compound 1m was obtained in 57% yield.

Compound 1i: mp 187 °C (*n*-pentane); IR (Nujol) cm⁻¹ 3370, 1690, 1640; ¹H NMR (CDCl₃) δ 1.3 (9 H, s, *t*-Bu), 5.06 (1 H, br s, NH), 6.83 (1 H, d, arom, *J* = 6.0 Hz), 7.26 (10 H, m, arom), 7.43 (1 H, pseudo-q, arom *J* = 6.0 Hz), 7.6 (1 H, br s, arom); mass spectrum calcd for C₂₄H₂₃NO, *m/e* 341.43, found *m/e* 341, *m/e* (relative intensity) 341 (M⁺, 33), 310 (100), 293 (27). Anal. Calcd for C₂₃H₂₃NO: C, 84.42; H, 6.79; N, 4.10. Found: C, 84.50; H, 6.85; N, 4.15.

Compound 1m: mp 182 °C (ligroin 80-100 °C); IR (Nujol) cm⁻¹ 1710, 1630; ¹H NMR (CDCl₃) δ 1.3 (9 H, s, *t*-Bu), 2.98 (3 H, s, Me), 6.78 (1 H, d, arom, *J* = 6.5 Hz), 7.26 (10 H, m, arom), 7.56

(1 H, pseudo-q, arom, *J* = 6.5 Hz, *J* = 2.0 Hz), 7.56 (1 H, d, arom, *J* = 2.0 Hz); mass spectrum calcd for C₂₅H₂₅NO, *m/e* 355.46, found *m/e* 355, *m/e* (relative intensity) 355 (M⁺, 71), 339 (26), 324 (100), 300 (29), 252 (52). Anal. Calcd for C₂₅H₂₅NO: C, 84.46; H, 7.09; N, 3.94. Found: C, 84.35; H, 7.15; N, 4.05.

Synthesis of the Dimers 4, 5, and 6. FeCl₃ (6 mmol in 20 mL of MeCN) was added dropwise at room temperature to a solution of 1e (1 mmol in 20 mL of MeCN) with magnetic stirring. After 2 h the reaction mixture was poured into water (100 mL) and extracted with benzene (2 × 50 mL). The benzene layer was separated, dried on Na₂SO₄, and chromatographed on a column of silica gel eluted with benzene. The second yellow eluate was compound 6 (30% yields). When 1k was treated in the same way, compound 5 was isolated in 40% yield as the first yellow eluate and compound 4 was obtained in 45% yield as the second yellow eluate.

Compound 4: mp 303 °C (benzene); IR (Nujol) cm⁻¹ 1690, 1625; ¹H NMR (CDCl₃) δ 2.89 (6 H, s, Me), 6.94 (2 H, d, arom, *J* = 9.0 Hz), 7.25-7.46 (20 H, m, arom), 7.78 (2 H, pseudo-q, arom, *J* = 9.0 Hz, *J* = 2.0 Hz), 7.82 (2 H, d, arom, *J* = 2.0 Hz); mass spectrum calcd for C₄₂H₃₂N₂O₂, *m/e* 596.69, found *m/e* 596, *m/e* (relative intensity) 596 (M⁺, 44), 595 (100), 567 (61), 489 (33), 268 (83), 232 (83). Anal. Calcd for C₄₂H₃₂N₂O₂: C, 84.53; H, 5.40; N, 4.69. Found: C, 84.26; H, 5.45; N, 4.76.

Compound 5: mp 310 °C (ligroin 100-135 °C); IR (Nujol) cm⁻¹ 1700, 1630; ¹H NMR (CDCl₃) δ 2.9 (3 H, s, Me), 3.37 (3 H, s, Me), 6.92 (1 H, d, arom, *J* = 9.0 Hz), 7.22-7.44 (20 H, m, arom), 7.66-7.80 (4 H, m, arom); mass spectrum calcd for C₄₂H₃₁N₂O₂Cl, *m/e* 631.12, found *m/e* 631, *m/e* (relative intensity) 630 (M⁺, 33), 629 (100), 601 (86). Anal. Calcd for C₄₂H₃₁N₂O₂Cl: C, 79.92; H, 4.95; N, 4.43. Found: C, 79.94; H, 4.90; N, 4.41.

Compound 6: mp 330 °C (CH₂Cl₂/*n*-hexane); IR (Nujol) cm⁻¹ 3340, 1785, 1638; ¹H NMR (CDCl₃) δ 5.36 (1 H, br s, NH), 5.48 (1 H, br s, NH), 7.02 (1 H, d, arom, *J* = 9.0 Hz), 7.24-7.52 (20 H, m, arom), 7.67 (1 H, d, arom, *J* = 2.0 Hz), 7.72-7.84 (3 H, m, arom); mass spectrum calcd for C₄₀H₂₇N₂O₂Cl, *m/e* 603.07, found *m/e* 603, *m/e* (relative intensity) 603 (M⁺, 15), 601 (50), 573 (80), 272 (100). Anal. Calcd for C₄₀H₂₇N₂O₂Cl: C, 79.80; H, 4.47; N, 4.65. Found: C, 79.88; H, 4.48; N, 4.55.

Radical Cations Originated by Chemical Oxidation. Indoxyl (1 mL of a 0.1 M solution in MeCN) and I₂/AgClO₄ (1 mL of a solution 0.1 M in MeCN) were put in one of the two legs of an inverted U cell,¹⁷ degassed with nitrogen, mixed, and transferred in the ESR cavity at room temperature.

ESR Spectra. The ESR spectra were simulated with a program written for a Wax computer, that uses a laurentzian function with a line width adjusted every time to match the experimental one.

McLachlan Spin Density Distributions. The spin density distributions were calculated by a computer program with the following values: $h_N = 1.5$; $K_{CN} = 1.0$; $K_{CC} = 1.0$; $K_{C_3-C_9} = 0.9$; $K_{CO} = 1.6$; $h_O = 1.5$; $\lambda = 1.2$.

Electrochemical Measurements. Apparatus and Procedures. MeCN and Et₄NClO₄ were purified as already described in the literature.⁹ The cell, the electrodes, the apparatus, and procedures employed have been reported elsewhere.⁹

Acknowledgment. We thank the Ministero della Pubblica Istruzione for financial support.

Registry No. 1a, 3920-67-0; 1b, 65817-64-3; 1c, 65817-65-4; 1d, 71149-34-3; 1e, 1922-77-6; 1f, 54451-06-8; 1g, 81235-53-2; 1h, 75654-78-3; 1i, 94137-30-1; 1j, 81235-52-1; 1k, 81235-51-0; 1l, 58863-88-0; 1m, 94137-31-2; 2m⁺, 94137-35-6; 3a⁺, 94293-85-3; 3b⁺, 94293-86-4; 3c⁺, 94293-89-7; 3d⁺, 94293-87-5; 3e⁺, 94293-88-6; 3h⁺, 94293-92-2; 3j⁺, 94293-91-1; 3k⁺, 94293-90-0; 3l⁺, 94293-93-3; 4, 94137-32-3; 5, 94137-36-7; 6, 94137-37-8; 7⁺, 94137-33-4; 9, 2989-63-1; 10, 3558-24-5; 11, 86453-84-1; 12⁺, 94137-38-9; 13⁺, 94137-34-5.

(13) Shine, H. J.; Wu, S.-M. *J. Org. Chem.* 1979, 44, 3310.

(14) Berti, C.; Greci, L.; Marchetti, L. *J. Chem. Soc., Perkin Trans. 2* 1979, 233.

(15) Colonna, M.; Greci, L.; Marchetti, L.; Andreotti, G. D.; Bocelli, G.; Sgarabotto, P. *J. Chem. Soc., Perkin Trans. 2* 1976, 309.

(16) Döpp, D.; Greci, L.; Nour-el-Din, A. M. *Chem. Ber.* 1983, 116, 2049.

(17) Russel, G. A.; Janzen, E. G.; Strom, E. T. *J. Am. Chem. Soc.* 1964, 86, 1806.

(18) McLachlan, A. D. *Mol. Phys.* 1960, 3, 233.