

## AMINO-INDOLE RADICAL CATIONS—II STABILITY AND ELECTRON TRANSFER REACTIONS

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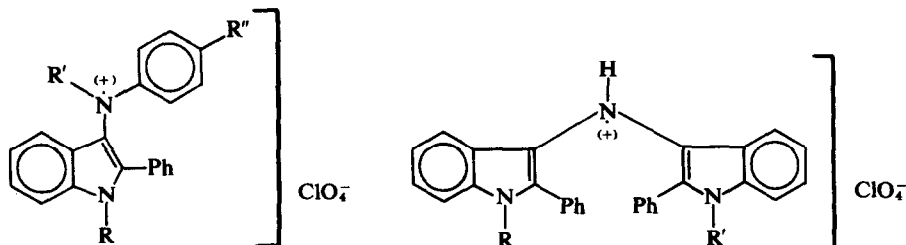
**Abstract**—2-Phenyl-3-aryl-amino indole and bis-indolyl-amine radical cations show different stabilities depending on the possibility of their being convertible into the corresponding imino-compounds. The route of this decomposition is demonstrated and the synthesis of some new amines and the corresponding radical cations is reported. Electron transfer reactions between amino-indoles and tris-(*p*-bromophenyl)-amminium perchlorate are also reported.

Amino-indole radical cations **1a, b, c, d, e, f, g** and **2a** have been previously prepared,<sup>1</sup> and it was found that radical salts **1c, e, f** and **2a** are stable enough to be isolated, while radicals **1a, b, d** are only detectable in an ESR cavity when generated *in situ* by appropriate oxidation of the corresponding amines, the signal generally disappearing in a few minutes. No determination was made of the radical concentrations in **1c, e, f** and **2a**; this work deals with a study of the stability of such radicals and of their decomposition routes. ESR and UV measurements as well as synthetic work were carried out.

### RESULTS AND DISCUSSION

When radical **2a** was prepared *in situ* without any particular care in excluding air from the ESR cell, but only bubbling N<sub>2</sub> through the solution, an ESR signal could be seen whose intensity decreased in time until a minimum unchangeable value was reached (Fig 1). However, if oxygen was carefully excluded, a stable, higher intensity signal was ob-

served. If radical **2a** was isolated as a solid and its concentration determined immediately after preparation in a carefully deoxygenated MeCN solution with an ESR spectrometer, a concentration of about 60% was obtained; if the determination was repeated under the same conditions after some weeks a lower concentration was found and by repeating such determinations we obtained a concentration of less than 1% after three months. The newly prepared radicals **2b** and **c** (Table 1) show the same behaviour while in series *I* we found that stability is dependent on the substituent in the *p*-position, following the order *p*-OMe ~ *p*-NMe<sub>2</sub> >>> *p*-Me ~ *p*-H > *p*-Hal. On the contrary, if the previous determinations were made on radical **1f**, the following results were obtained: (i) the solid radical cation perchlorate dissolved in MeCN shows a concentration of 100% and its concentration did not change after 6 months; (ii) a MeCN solution of **1f** shows an unchangeable 100% concentration when tested repeatedly for some days. These observations are important, first be-



- 1a:** R = R' = R'' = H  
**b:** R = R' = H; R'' = Me  
**c:** R = R' = H; R'' = OMe  
**d:** R = R' = H; R'' = Br  
**e:** R = R' = H; R'' = NMe<sub>2</sub>  
**f:** R = H; R' = Me; R'' = OMe  
**g:** R = R' = Me; R'' = NMe<sub>2</sub>  
**h:** R = H; R' = Me; R'' = Cl

- 2a:** R = R' = H  
**b:** R = H; R' = Ph  
**c:** R = H; R' = Et

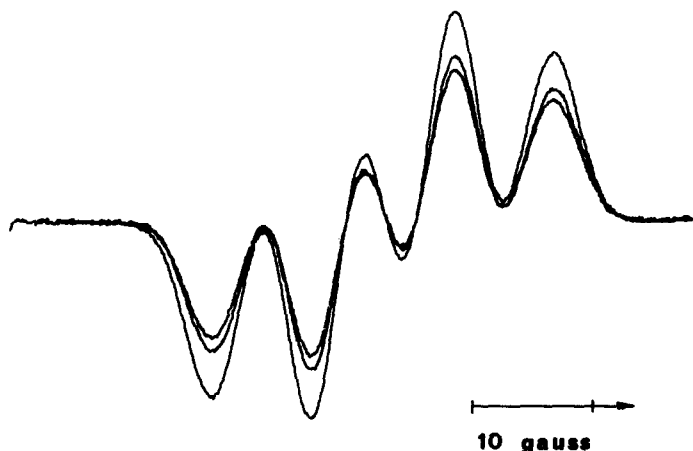


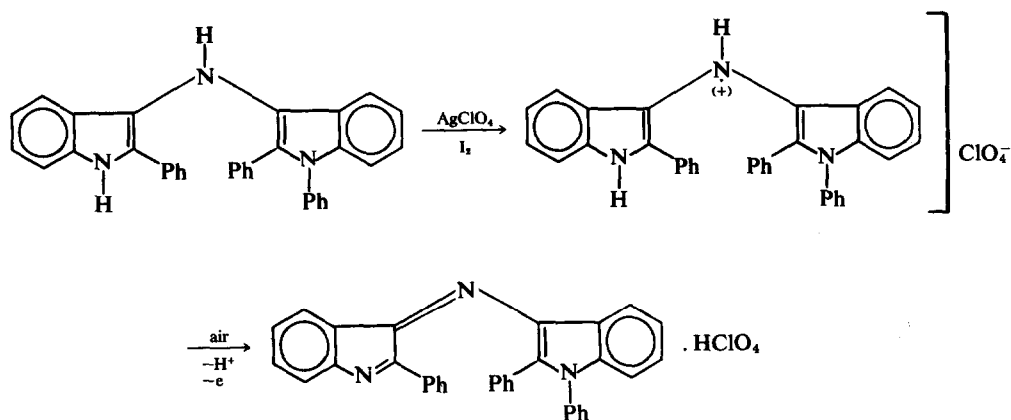
Fig 1. Experimental ESR spectrum of the radical cation **2a**, higher intensity: after 10 min; medium intensity: after 20 min; lower intensity: after 30 min.

Table 1

Compound	m.p. (solvent)	Analysis %		IR: $\nu, \text{cm}^{-1}$ (nujol)	Yield %
		Found	Calc.		
3,3'-bis-(1,2-diphenyl-1'-H-2'-phenyl)-indolyl-amine	166-7°	C, 86.12 H, 5.33 N, 8.75	$\text{C}_{34}\text{H}_{25}\text{N}_3$ C, 85.87 H, 5.30 N, 8.84	Indolic NH 3448	90
	benzene/light petroleum			Amine NH 3348	
3,3'-bis-(1 ethyl-2-phenyl-1'-H-2'-phenyl)-indolyl-amine	174°	C, 84.41 H, 5.81 N, 9.76	$\text{C}_{30}\text{H}_{25}\text{N}_3$ C, 84.28 H, 5.89 N, 9.83	Indolic NH 3428	88
	benzene/light petroleum			Amine NH 3328	
<b>2b</b>	240-50°	C, 70.88 H, 4.07 N, 7.01	$\text{C}_{34}\text{H}_{25}\text{N}_3\text{ClO}_4$ C, 71.02 H, 4.38 N, 7.30		82
	MeCN/light petroleum				
<b>2c</b>	205-10°	C, 68.26 H, 4.72 N, 7.87	$\text{C}_{30}\text{H}_{25}\text{N}_3\text{ClO}_4$ C, 68.37 H, 4.78 N, 7.97		63
	MeCN/light petroleum				

cause they allow us to consider radical cation **1f** as a new, absolutely stable radical with a 100% concentration, which can be used as a standard for concentration measurements of the other amino indole radical cations; next, because they allow us to elucidate the mechanism of decomposition of such radicals, which can be rationalized as below. The alternative route, through a neutral radical and

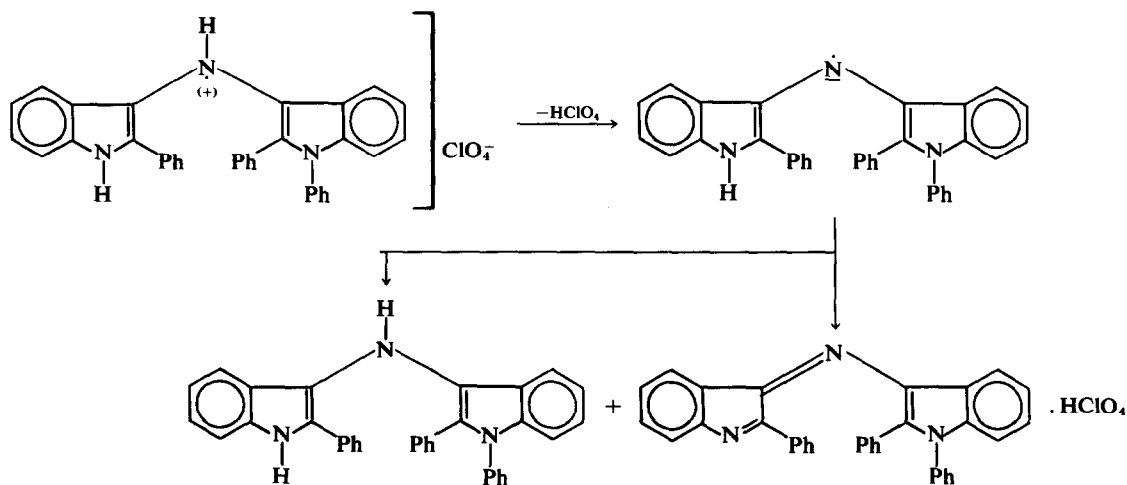
a disproportionation reaction cannot be considered, primarily because it does not involve oxygen, which is the necessary condition in order to destroy the radical cation, and then because no trace of the amine was found in the decomposition mixture; on the contrary, the perchlorate of the 1,2-diphenyl-3-[(2-phenyl-3H-indol-3-ylidene)amino]-indole was found, and consequently prepared in an indepen-



dent way: it shows no ESR signal, but it has the same properties and the same absorption spectrum (Fig 2; discussion later) as the decomposed radical cation. At this point we can state that: (i) amino-indole radical cations of the form 1 where  $\text{R}' = \text{H}$  have different stability, depending on the particular substituent in the *p*-position in the phenyl ring;<sup>2</sup> (ii) the final product in the decomposition of radical 1a, b, c, d, e and 2a, b, c, is the corresponding imino-compound;<sup>3</sup> (iii) when the amino-hydrogen is substituted with an alkyl group, the radical stability is enhanced and if the two effects, N-methylation and the presence of electron donor *p*-substituents, act on the same compound, an indefinitely stable radical occurs; (iv) N-methylation is not alone responsible for radical stability: as a matter of fact, radical 1h is not indefinitely stable like radical 1f and the electron withdrawing *p*-substituent seems to be the reason for such instability. In this case a different decay mechanism must occur and its study is the object of our current investigations.

The clearest evidence for some of these statements comes from a study of the absorption spectra of the species involved. Fig 2 shows the absorption spectrum of an  $\text{MeCN}/\text{C}_2\text{H}_4\text{Cl}_2$  solution of the radical cation 2b produced *in situ* (line B), which is indicated as a mixture of the perchlorates of the radical and of the non-radical base because of the spontaneous partial oxidation of the radical cation discussed previously. It shows two maxima at 647 and 490  $\mu\text{m}$ : we excluded the maxima whether attributable to the bis-indolyl-amine with characteristic maxima at 247 and 306  $\mu\text{m}$ \* or to the free base, with a maximum at 545  $\mu\text{m}$  (dotted line). Curve A reproduces the absorption spectrum of the perchlorate of the non-radical 1,2-diphenyl-3-[(2-phenyl-3H-indol-3-ylidene)amino]indole, with a single maximum at 647  $\mu\text{m}$ , characterized by a lower absorbance than that of the radical cation. Comparison of the spectra clearly shows that both maxima are characteristic of the radical cation (that at 647  $\mu\text{m}$  because of its higher absorbance). As shown in Fig. 3 both maxima decrease with time, leading to the disappearance of the maximum at

\*For analogous compounds see ref. 3.



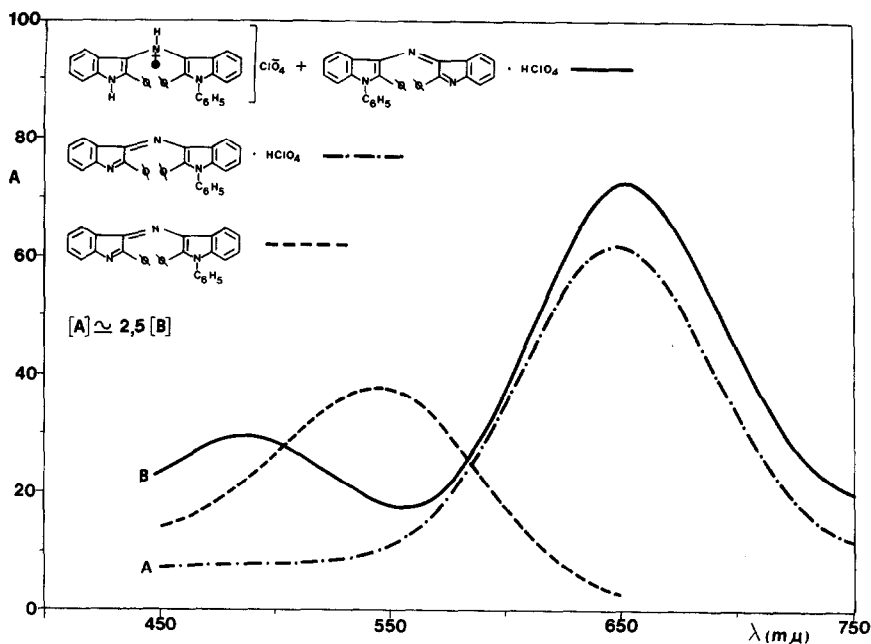


Fig 2. Absorption spectra.

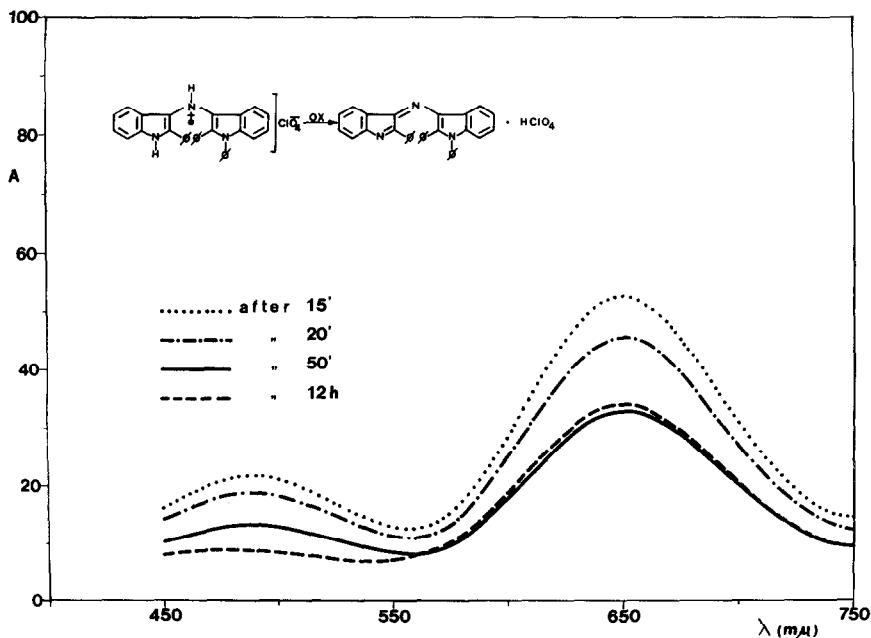


Fig 3. Absorption spectra of the amino-indole radical cation.

490  $m\mu$  and to a lowering of the other one to values characteristic of the non-radical base.

Finally, we would like to report a new method of generating amine-indole radical cations: it is known<sup>4</sup> that the tris(*p*-bromophenyl)-amminium perchlorate is a good one-electron oxidizing agent for

many organic substrates. We found that with our amines it gives an extremely easy electron transfer reaction<sup>5</sup> of similar type. The results of such reactions are reported in Table 2, yields being for purified products. The reaction is extremely simple and no traces of the starting indole amine or of the

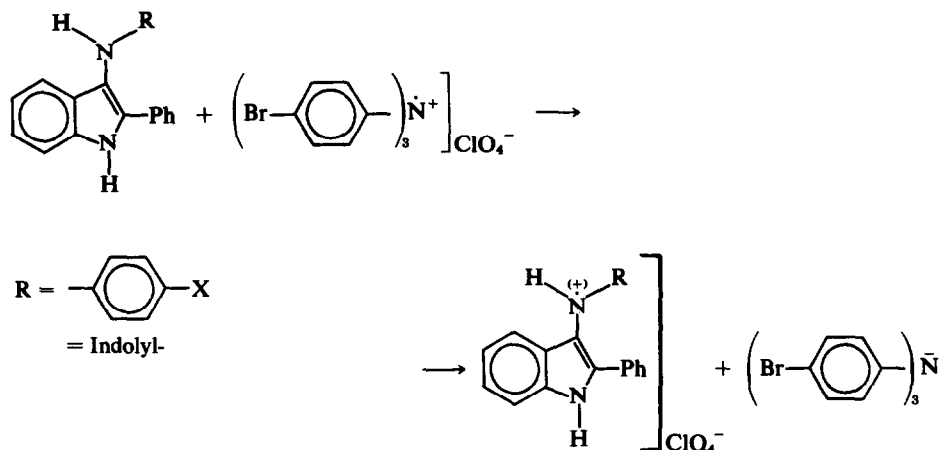


Table 2. Electron transfer reactions with tris-(*p*-bromophenyl)-amminium perchlorate

Amine	Radical	Yields %
2-phenyl-3-( <i>p</i> -dimethylamino-phenyl)-amine indole	1e	48
2-phenyl-3-( <i>p</i> -anisidyl)-amine indole	1c	43
3,3'-bis-indolyl-amine	2a	52
3,3'-bis-1-ethyl-2-phenyl-2'-phenyl-amine indole	2c	57
3,3'-bis-1,2-diphenyl-2'-phenyl-amine indole	2b	63

tris-(*p*-bromophenyl)-amminium cation were found at the end. The amino indole radical cations so produced show the same properties and characteristics as when generated by oxidation with the Gomberg reagent, thus excluding the possibility that the particular synthesis is responsible for their different stability.

#### EXPERIMENTAL

**3,3'-Bis-indolyl-amines.** 1.00 g of the 1-substituted-2-phenyl-[(2-phenyl-3H-indol-3-ylidene)amino]-indole<sup>6</sup> dissolved in 100 ml of anhydrous benzene was hydrogenated at room temp and at 2 atm pressure on 0.15 g of Pt/C 5%. After reduction was complete, the catalyst was filtered and most of the solvent evaporated. The residue was warmed and light petroleum added. A white precipitate of the amine separated and was collected. Analytical data are reported in Table 1.

**Bis-indolyl-amine radical cation perchlorates.** To a stirred solution of 1.5 mM of the amine in 25 ml of MeCN, were added 1.6 mM of AgClO<sub>4</sub>, dissolved in 15 ml of MeCN, drop by drop at room temp. The initial colourless solution of the amine turned deep green, while a silver mirror was formed. After ten min the solution was filtered and 200 ml of ether were added: the perchlorate of the radical cation separated as small brown pellets.

**1,2-Diphenyl-3-[(2-phenyl-3H-indol-3-ylidene)amino]-indole perchlorate.** To a stirred solution of 0.47 g (1 mM) of the base dissolved in 30 ml of MeCN, 0.5 ml (3 mM) of 60% HClO<sub>4</sub> were added. After five min the salt was filtered and purified from MeCN/ether: m.p. 235–45°

(100%). (Found: C, 70.91; H, 4.31; N, 7.38; Calc. for C<sub>34</sub>H<sub>24</sub>N<sub>3</sub>ClO<sub>4</sub>, C, 71.14; H, 4.22; N, 7.32%). This compound shows no ESR signal.

**2-Phenyl-3-(*N*-methyl-*N*-*p*-Cl-phenyl)-amine-indole.** 2.53 g of 2-phenyl-3-(*N*-*p*-Cl-phenyl)-amine indole,<sup>3</sup> 10 ml of MeOH and 3 ml of MeI were heated at 140° for 2 h in a 500 ml autoclave in a N<sub>2</sub> atmosphere. After cooling, the mixture was dissolved in CHCl<sub>3</sub> and treated in a dropping funnel with aqueous ammonia. The CHCl<sub>3</sub> layer was dried (Na<sub>2</sub>SO<sub>4</sub>), the solvent evaporated and the residue dissolved in a very small amount of benzene and treated on a SiO<sub>2</sub> column by elution with a mixture of light petroleum/EtOAc 9:1. The head fraction of the column was repeatedly crystallized from 60–80° ligroin to m.p. 162–3°; (40%). (Found C, 76.01; H, 4.97; N, 8.07; Calc. for C<sub>21</sub>H<sub>17</sub>N<sub>2</sub>Cl: C, 76.01; H, 5.16; N, 8.44%). IR spectrum shows only one N–H band at 1495 cm<sup>-1</sup>.

**Radicals obtained directly in the ESR spectrometer cavity.** These were prepared using an inverted U cell described by Russell<sup>7</sup> *et al.* and equipped with a VARIAN aqueous sample flat cell. One leg of the cell was filled with 1 ml of a 0.0015 M solution in MeCN of the amine, the other with 1 ml of a 0.0015 M solution in MeCN of AgClO<sub>4</sub> or with 1 ml of a solution 0.0015 M in AgClO<sub>4</sub> and 0.00075 M in I<sub>2</sub> (Gomberg reagent). After mixing, the solution was forced into the cell and the latter inserted in the cavity.

**Electron transfer reactions.** 0.5 mM of the tris-(*p*-bromophenyl)-amminium perchlorate<sup>8</sup> were dissolved in 10 ml of CH<sub>2</sub>Cl<sub>2</sub>, cooled at 0–5° and added to a solution of 0.5 mM of the amine in 15 ml of CH<sub>2</sub>Cl<sub>2</sub>, previously cooled to the same temperature. The colour, initially blue, turned to deep green: the mixture was stirred at 0–5° for 40 min, then ether was added. The perchlorate of the radical cation precipitated (Table 2). After filtration, the solution was evaporated to dryness and the residue, dissolved in benzene and eluted with benzene on an Al<sub>2</sub>O<sub>3</sub> column, gave the tris-(*p*-bromo-phenyl)-amine,<sup>9</sup> m.p. 144°.

**Spectra.** ESR spectra were recorded on a VARIAN E-4; UV and visible spectra were recorded on a Beckman DK-2A; IR spectra were recorded on a Perkin-Elmer, model 257 IR. All solvents were dried by conventional methods.

#### REFERENCES

- <sup>1</sup>P. Bruni, M. Colonna and L. Greci, *Tetrahedron* **27**, 5893 (1971).

- <sup>2</sup>R. N. Adams and Co., *J. Am. Chem. Soc.* **88**, 3498 (1966).
- <sup>3</sup>L. Marchetti, L. Greci and G. Tosi, *Gazz. Chim. Ital.* **100**, 770 (1970).
- <sup>4</sup>C. E. H. Bawn, F. A. Bell and A. Ledwith, *Chem. Comm.* 599 (1968).
- <sup>5</sup>A. Ledwith, *Acc. Chem. Res.* **5**, 133 (1972).
- <sup>6</sup>M. Colonna and L. Greci, *Gazz. Chim. Ital.* (in press.)
- <sup>7</sup>G. A. Russell and Co., *J. Am. Chem. Soc.* **86**, 1807 (1964).
- <sup>8</sup>F. A. Bell, A. Ledwith and D. C. Sherrington, *J. Chem. Soc. (C)* 2719 (1969).
- <sup>9</sup>T. N. Baker and Co., *J. Org. Chem.* **30**, 3714 (1965);  
H. Wieland, *Ber. Dtsch. Chem. Ges.* **40**, 4278 (1907).