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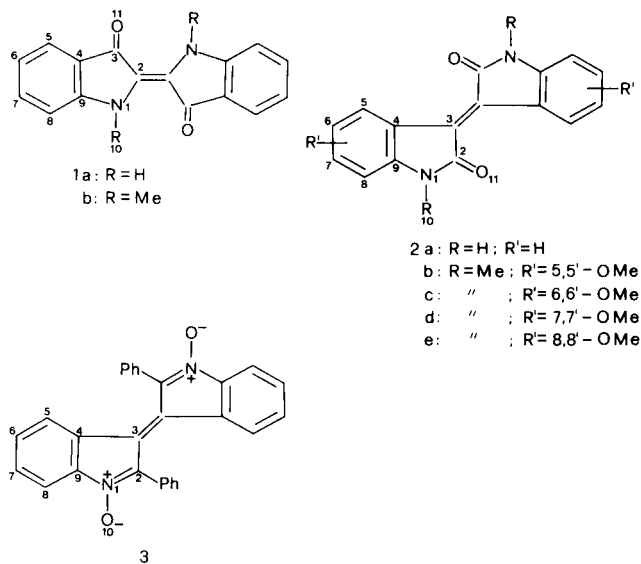
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Received March 2, 1981

*N,N'*-Dimethylisoidindigo and four methoxy derivatives have been synthesized and reduced to the corresponding radical anions by *t*-BuOK-DMSO. The epr spectra are reported and discussed.

*J. Heterocyclic Chem.*, **19**, 211 (1982).

It has been reported (1) that 1,1'-dimethyl-3,3'-dioxo-2,2'-bi-3*H*-indole (*N,N'*-dimethylindigo) is a good source of *N*-methylisatin radical anion, when treated with base in DMSO. No *N,N'*-dimethylindigo radical anion was thus observable under these conditions. Indigo itself, as well as isoidindigo, under the previous conditions yielded the indigo or isoidindigo radical anions (2-4). No work has been done to date on 1,1'-dimethyl-2,2'-dioxo- $\Delta^{3,3'}$ -bi-3*H*-indole (*N,N'*-dimethylisoidindigo) in this regard, even if it has been postulated the existence of intermediate neutral and anion radicals of *N,N'*-dimethylisoidindigo in the reaction of 1-methyl-2-oxindole with nitroso compounds (5).



In the present work we demonstrate that *N,N'*-dimethylisoidindigo can be easily reduced to its anion radical when treated with potassium *t*-butoxide in DMSO, and we discuss the spectrum obtained by observing the full series (2b-e) of the corresponding benzomethoxy derivatives.

Compounds were prepared by oxidation of the corresponding 1-methyloxindoles (6) with freshly prepared lead dioxide in boiling benzene, a procedure that led to better yields (50-60%) than the one reported in the literature (7).

Contribution to the discussion is also obtained by

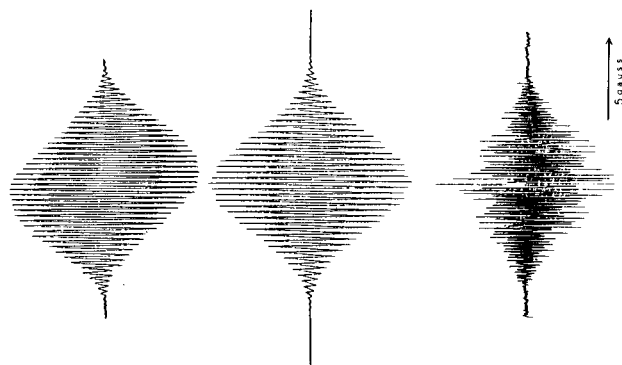


Figure 1. Experimental (top) and calculated (middle) epr spectrum of *N,N'*-dimethylisoidindigo: experimental (bottom) epr spectrum of *N,N'*-dimethyl-6,6'-dimethoxyisoidindigo.

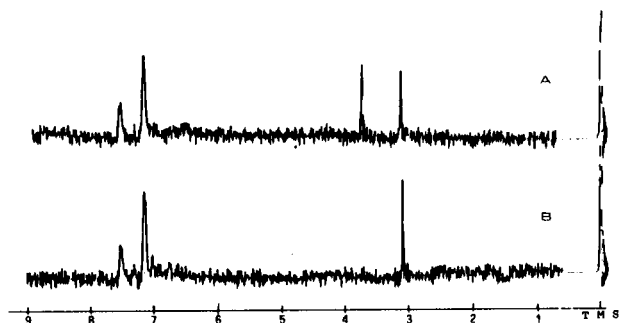


Figure 2. Nuclear magnetic resonance spectra (in pyridine- $d_5$ ) of the 6,6'-dimethoxy derivative, 2c (A) and of *N,N'*-dimethylisoidindigo 2a (B).

Mc'Lachlan MO calculations (8). Experimental epr splitting constants for all the compounds are reported in the Table together with spin density values for the unsubstituted molecule. In Figure 1 are reported the epr spectrum of the unsubstituted *N,N'*-dimethylisoidindigo radical anion (top), that has been exactly reproduced (middle) using parameters listed in Table, and the one of the 6,6'-dimethoxy derivative (2c). For comparison the epr

Table

EPR Splitting Constants and Mc'Lachlan Spin Densities for *N,N'*-dimethylisoidigo and its Methoxybenzo Derivatives.  
EPR Splitting Constants for the Indigo Radical Anions.

| Position | Unsubstituted<br><i>N,N'</i> -Dimethylisoidigo |                    | HFSC of Methoxy Derivatives<br>(gauss) |           |           |           | Indigo HFSC<br>(gauss) |       |
|----------|------------------------------------------------|--------------------|----------------------------------------|-----------|-----------|-----------|------------------------|-------|
|          | HFSC (gauss)                                   | Spin Densities (a) | <b>2b</b>                              | <b>2c</b> | <b>2d</b> | <b>2e</b> | a (b)                  | b (c) |
| 1        | 0.70                                           | -0.044             | 0.070                                  | 0.070     | 0.66      | 0.70      | 1.22                   | 0.67  |
| 2        |                                                | -0.0193            |                                        |           |           |           |                        |       |
| 3        |                                                | 0.1555             |                                        |           |           |           |                        |       |
| 5        | 1.40                                           | 0.0537             | 0.70 (d)                               | 1.50      | 1.67      | 1.30      | 0.68                   | 1.52  |
| 6        |                                                | -0.0083            |                                        | 0.20 (d)  |           |           | 0.68                   | 0.50  |
| 7        | 2.10                                           | 0.0918             | 2.90                                   | 2.90      |           | 2.20      | 2.30                   | 1.98  |
| 8        | 0.70                                           | -0.0313            | 0.70                                   |           | 1.00      |           | 0.68                   | 0.67  |
| 10       | 0.35                                           | 0.238              | 0.40                                   | 0.40      | 0.33      | 0.30      | 0.14                   | 0.20  |
| 11       |                                                | 0.1171             |                                        |           |           |           |                        |       |

(a) The following parameters were used:  $h_N = 1.19$ ,  $h_O = 0.84$ ,  $k_{CN} = 1.29$ ,  $k_{CO} = 1.36$ ;  $\lambda = 1.2$ . (b) See reference 3); values not attributed in the original work, the radical was obtained by reduction of indigo with hydrazobenzene in methanol containing sodium methoxide. (c) See reference 7): radical obtained in strongly alkaline ethanol. (d) OMe.

data for the indigo radical anion is listed in the Table as previously reported. Previously unknown nmr spectra of some compounds in pyridine- $d_5$  are reported in Figure 2.

A series of comments can be made on the experimental data. The observed splitting constants for *N,N'*-dimethylisoidigo radical anion are consistent with the values found by Bruin (9) in his work, where a correct interpretation of all the hyperfine splitting constants of the benzo protons has been reported.

The observation that the maximum unpaired electron density resides on the O=C-C=C-C=O chromophore is confirmed by Mc'Lachlan MO calculations. As a consequence, positions 7 and 7', 5 and 5', that bear the higher conjugation, being respectively *para* and *ortho* to the chromophore, show higher values of the  $a^H$  parameters. Spectra reveal no splitting constants attributable to the hydrogens in positions 6 and 6'. That is consistent with the low spin density found for this position. As a matter of fact a mean value of about 23 gauss for the  $Q_C$  parameter can be calculated from formula  $a^H = Q_C \rho_C$  using  $a^H$  and  $\rho_C$  values for atoms at position 5-7-8, from which an  $a^H$  of 0.2 gauss is obtained for the splitting of hydrogens bonded to carbon atoms in positions 6 and 6', that is certainly missed in the experimental spectrum showing a line width of the same magnitude. A similar situation was already found in the spectrum of the 1,1'-dioxy-2,2'-diphenyl- $\Delta^{3,3}$ -bi-3H-indole radical anion **3**. In both cases the positions involved (6-6' and 5-5', respectively) are *meta* to the group of largest unpaired electron density. The fact that in the latter case the six benzo protons, bearing no zero  $a^H$ , all appear equivalent, while in the case discussed in this work they show considerable differences certainly finds a valid explanation in the difference of the global spin density on the benzo rings that, from calculations, appears to be about 10% of the whole in the case of the 1,1'-dioxy-2,2'- $\Delta^{3,3}$ -bi-3H-indole radical anion and about 37% in that of the *N,N'*-dimethylisoidigo radical anion.

## EXPERIMENTAL

The epr spectra were recorded on a Varian Model E-4 EPR spectrometer using a deaired two legs inverted cell previously described (11). Samples (5 mmoles) and anhydrous DMSO were placed on one leg while the other was filled with 0.05 g of anhydrous *t*-BuOK. After degassing with a flow of dry nitrogen (20 minutes), the reagents were mixed and transferred into the epr cell.

The nmr and ir spectra were recorded on a Perkin-Elmer Model R12B NMR spectrometer and a Perkin-Elmer Model 257 IR spectrophotometer, respectively. All solvents were RP grade Merk reagents.

### General Procedure.

*N,N'*-dimethylisoidigo **2a** (12) and its benzomethoxy derivatives **2b-e** were prepared with the following procedure: 0.02 moles of the oxindole (12) or of the substituted oxindole (13), prepared according to the literature, were mixed with 2 g of freshly prepared lead dioxide in 40 ml of anhydrous benzene. The mixture was refluxed for 30 minutes, cooled and then filtered. The solution was evaporated and the residue was passed through an alumina column using benzene as the solvent. The main fraction contained the *N,N'*-dimethylisoidigos with the yield in the range of 60%.

#### 1,1'-Dimethyl-2,2'-dioxo-5,5'-dimethoxy- $\Delta^{3,3}$ -bi-3H-indole (**2b**).

This compound had mp 250-251°; ir (nujol): 1685  $\text{cm}^{-1}$  (C=O); nmr (ppm, pyridine- $d_5$ ):  $\delta$  3.0 (s, -CH<sub>3</sub>, 6H), 3.8 (s, -OCH<sub>3</sub>, 6H).

Anal. Calcd. for C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>: C, 68.55; H, 5.19; N, 7.99. Found: C, 68.33; H, 5.24; N, 7.90.

#### 1,1'-Dimethyl-2,2'-dioxo-6,6'-dimethoxy- $\Delta^{3,3}$ -bi-3H-indole (**2c**).

This compound had mp 235-238°; ir (nujol): 1675  $\text{cm}^{-1}$  (C=O); nmr (ppm, pyridine- $d_5$ ):  $\delta$  3.2 (s, -CH<sub>3</sub>, 6H), 3.8 (s, -OCH<sub>3</sub>, 6H).

Anal. Calcd. for C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>: C, 68.55; H, 5.19; N, 7.99. Found: C, 68.28; H, 5.14; N, 7.93.

#### 1,1'-Dimethyl-2,2'-dioxo-7,7'-dimethoxy- $\Delta^{3,3}$ -bi-3H-indole (**2d**).

This compound had mp 265-267°; ir (nujol): 1680  $\text{cm}^{-1}$  (C=O); nmr (ppm, pyridine- $d_5$ ):  $\delta$  3.2 (s, -CH<sub>3</sub>, 6H), 3.9 (s, -OCH<sub>3</sub>, 6H).

Anal. Calcd. for C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>: C, 68.55; H, 5.19; N, 7.99. Found: C, 68.40; H, 5.20; N, 7.91.

#### 1,1'-Dimethyl-2,2'-dioxo-8,8'-dimethoxy- $\Delta^{3,3}$ -bi-3H-indole (**2e**).

This compound had mp 253-255°; ir (nujol): 1678  $\text{cm}^{-1}$  (C=O); nmr (ppm, pyridine- $d_5$ ):  $\delta$  3.2 (s, -CH<sub>3</sub>, 6H), 3.8 (s, -OCH<sub>3</sub>, 6H).

Anal. Calcd. for C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>: C, 68.55; H, 5.19; N, 7.99. Found: C, 68.61; H, 5.07; N, 8.10.

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