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# Studies in Tertiary Amine Oxides

## Part V†—Carbon-13 Nuclear Magnetic Resonance Spectra of some *N*-Aryl Tertiary Amines, the Corresponding *N*-Oxides and the Meisenheimer Rearrangement Products

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The carbon-13 NMR spectra of some *N*-(2- or 4-nitrophenyl) tertiary amines and their corresponding *N*-oxides have been analysed. These *N*-oxides undergo thermal rearrangement to *O*-arylhydroxylamines, for which the <sup>13</sup>C NMR spectral assignments were also carried out. The *N*-oxidation effect on the aromatic and aliphatic fragments is calculated.

### INTRODUCTION

The chemistry of tertiary amine oxides has received considerable attention, partly because they play an important role in a number of biological systems<sup>1</sup> and partly because of their interesting thermal rearrangement to the substituted hydroxylamines. The isomerization of tertiary amine oxides in which a certain group migrates from N to O (e.g.  $R_1R_2R_3N \rightarrow O \rightarrow R_1R_2N-O-R_3$ ) is known as the Meisenheimer rearrangement.<sup>2</sup> The type of groups which can migrate to oxygen include allyl,<sup>3</sup> benzyl,<sup>4</sup> neopentyl,<sup>5</sup> homoadamantyl<sup>6</sup> and tetrachloropyridyl.<sup>7</sup> The benzene nucleus can undergo migration during the thermolysis of substituted aniline *N*-oxides<sup>8</sup> and, furthermore, a number of *N*-aryl cyclic amine *N*-oxides have recently been shown to undergo isomerization to *O*-arylhydroxylamines<sup>9</sup> (Scheme 1).

There are few tertiary *N*-oxides for which <sup>13</sup>C NMR spectral data are known. This paper describes the <sup>13</sup>C NMR spectroscopy of the amines (**1**, **2**) their *N*-oxides (**3**, **4**) and their rearrangement products (**5**, **6**), and the effect of the *N*-oxide on the chemical shifts of various carbons in the above compounds.

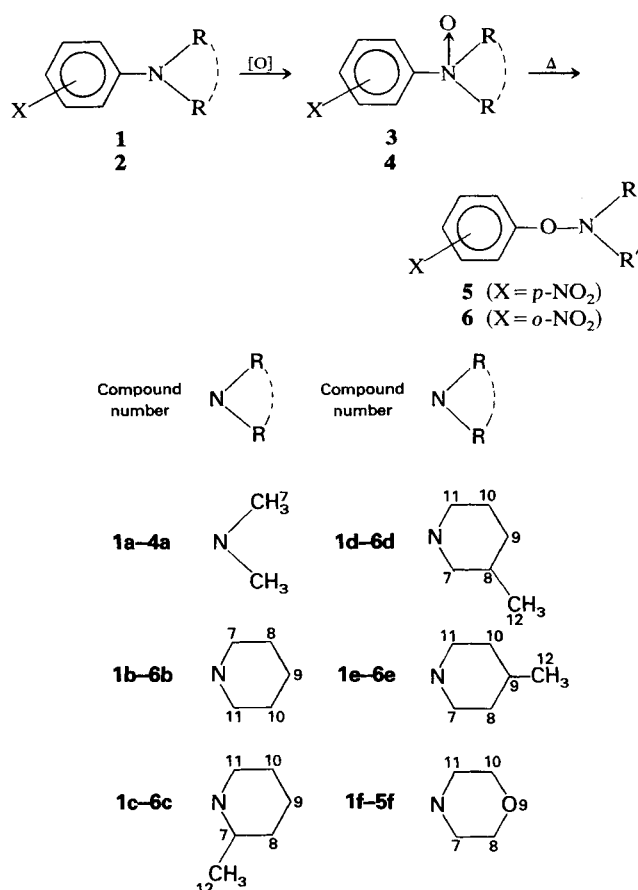
### RESULTS

#### The assignment of the <sup>13</sup>C chemical shifts for the saturated heterocyclic ring

This was achieved for compounds **1–6** (Scheme 1) by using the reported values of the <sup>13</sup>C chemical shifts and the coupling pattern for analogous compounds.<sup>10,11</sup>

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† For Part IV, see Ref. 9.



Scheme 1. The tertiary amines, the *N*-oxides and their rearrangement products.

#### The assignment of the <sup>13</sup>C chemical shifts for the aromatic ring

##### *N*-Aryl-*tert*-amines **1** and **2**.

(a) *N*-(4-Nitrophenyl)amines **1a–1f**: the broad band proton decoupled <sup>13</sup>C NMR spectra of the aromatic carbons in **1a–1f** (Table 1) were analysed using the

**Table 1. Carbon-13 chemical shift assignments relative to TMS for *N*-(4-nitrophenyl)amines (1)<sup>a</sup>**

| Compound No.       | C-1   | C-2   | C-3   | C-4   | C-5   | C-6   | C-7  | C-8  | C-9  | C-10 | C-11 | C-12 |
|--------------------|-------|-------|-------|-------|-------|-------|------|------|------|------|------|------|
| <b>1a</b>          | 154.4 | 110.4 | 126.1 | 137.3 | 126.1 | 110.4 | 40.2 | —    | —    | —    | —    | —    |
| Calc. <sup>b</sup> | 156.5 | 113.6 | 123.2 | 136.7 | 123.2 | 113.6 |      |      |      |      |      |      |
| <b>1b</b>          | 155.1 | 112.4 | 126.0 | 137.8 | 126.0 | 112.4 | 48.4 | 25.4 | 24.2 | 25.4 | 48.4 | —    |
| <b>1c</b>          | 154.8 | 112.3 | 126.1 | 137.5 | 126.1 | 112.3 | 49.8 | 30.5 | 18.4 | 25.5 | 41.8 | 14.5 |
| <b>1d</b>          | 154.9 | 112.4 | 126.1 | 137.6 | 126.1 | 112.4 | 55.2 | 30.7 | 32.8 | 24.7 | 47.9 | 19.1 |
| <b>1e</b>          | 154.9 | 112.5 | 126.1 | 137.6 | 126.1 | 112.5 | 47.8 | 33.5 | 30.7 | 33.5 | 47.8 | 21.6 |
| <b>1f</b>          | 155.1 | 112.7 | 125.9 | 140.0 | 125.9 | 112.7 | 47.2 | 66.4 | —    | 66.4 | 47.2 | —    |
| Calc. <sup>c</sup> | 155.3 | 115.2 | 122.8 | 138.4 | 122.8 | 115.2 |      |      |      |      |      |      |

<sup>a</sup> The numbering of the carbon atoms corresponds with that in Scheme 1.<sup>b</sup> Calculated values were obtained using the NO<sub>2</sub> effect on the <sup>13</sup>C chemical shift of the aromatic carbons in *N,N*-dimethylaniline [ $\delta$ (CDCl<sub>3</sub>), C-1 = 150.7; C-2,6 = 112.7; C-3,5 = 129.8; C-4 = 116.0 and C-7 = 40.3 ppm].<sup>c</sup> Calculated values were obtained using the NO<sub>2</sub> effect on the <sup>13</sup>C chemical shift of the aromatic carbons of *N*-phenylmorpholine [ $\delta$ (CDCl<sub>3</sub>) C-1 = 149.5; C-2,6 = 114.3; C-3,5 = 127.6; C-4 = 118; C-7,11 = 48.7 and C-8 = 66.0 ppm].**Table 2. Carbon-13 chemical shift assignments relative to TMS for *N*-(2-nitrophenyl)amines (2)<sup>a</sup>**

| Compound No.       | C-1   | C-2   | C-3   | C-4   | C-5   | C-6   | C-7  | C-8  | C-9  | C-10 | C-11 | C-12  |
|--------------------|-------|-------|-------|-------|-------|-------|------|------|------|------|------|-------|
| <b>2a</b>          | 146.2 | 139.5 | 126.5 | 118.3 | 133.2 | 117.9 | 42.3 | —    | —    | —    | —    | —     |
| Calc. <sup>b</sup> | 145.9 | 132.7 | 124.2 | 117.6 | 134.8 | 113.6 |      |      |      |      |      |       |
| <b>2b</b>          | 147.1 | 142.5 | 125.8 | 121.3 | 133.2 | 120.8 | 53.2 | 26.1 | 24.1 | 26.1 | 53.2 | —     |
| <b>2c</b>          | 145.8 | 147.7 | 125.0 | 124.0 | 132.2 | 123.5 | 55.0 | 33.5 | 22.7 | 26.2 | 53.0 | 18.3  |
| <b>2d</b>          | 146.9 | 142.7 | 126.0 | 121.0 | 133.4 | 120.6 | 59.7 | 31.1 | 32.6 | 25.5 | 52.6 | 19.11 |
| <b>2e</b>          | 147.0 | 142.8 | 126.0 | 121.0 | 133.4 | 120.6 | 52.2 | 34.3 | 30.6 | 34.3 | 52.2 | 21.8  |
| <b>2f</b>          | 146.2 | 144.8 | 125.8 | 122.5 | 133.5 | 121.3 | 52.3 | 66.9 | —    | 66.9 | 52.3 | —     |
| Calc. <sup>c</sup> | 144.7 | 134.3 | 122.8 | 119.3 | 133.4 | 115.2 |      |      |      |      |      |       |

<sup>a</sup> The numbering of the carbon atoms corresponds with that in Scheme 1.<sup>b,c</sup> See Table 1 footnotes.**Table 3. Carbon-13 chemical shift assignments relative to TMS for *N*-(4-nitrophenyl)amine *N*-oxides (3)<sup>a</sup>**

| Compound No.       | C-1              | C-2   | C-3   | C-4   | C-5   | C-6   | C-7    | C-8    | C-9  | C-10   | C-11 | C-12   |
|--------------------|------------------|-------|-------|-------|-------|-------|--------|--------|------|--------|------|--------|
| <b>3a</b>          | 158.2            | 122.0 | 125.0 | 148.2 | 125.0 | 122.0 | 62.6   | —      | —    | —      | —    | —      |
| Calc. <sup>b</sup> | 160.4            | 120.9 | 123.2 | 148.8 | 123.2 | 120.0 |        |        |      |        |      |        |
| <b>3b</b>          | 161.2            | 122.5 | 124.5 | 147.9 | 124.5 | 122.5 | 69.2   | 21.3   | 21.9 | 21.3   | 69.2 | —      |
| <b>3c</b>          | 159.3            | 122.7 | 124.2 | 147.3 | 124.2 | 122.7 | 74.3   | 26.4   | 16.3 | 20.9   | 59.3 | 59.9   |
|                    | (u) <sup>c</sup> | (u)   | (u)   | (u)   | (u)   | (u)   | (71.3) | (28.7) | —    | (21.0) | —    | (15.2) |
| <b>3d</b>          | 160.8            | 122.4 | 124.5 | 147.9 | 124.5 | 122.4 | 75.2   | 26.9   | 30.5 | 21.2   | 68.7 | 18.6   |
| <b>3e</b>          | 161.1            | 122.4 | 124.5 | 148.0 | 124.5 | 122.4 | 69.1   | 29.4   | 29.1 | 29.4   | 69.1 | 21.4   |
| <b>3f</b>          | 159.6            | 122.3 | 124.9 | 148.1 | 124.9 | 122.3 | 68.0   | 62.2   | —    | 62.2   | 68.0 | —      |

<sup>a</sup> The numbering of the carbon atoms corresponds with that in Scheme 1.<sup>b</sup> Calculated values were obtained using the NO<sub>2</sub> effect on the <sup>13</sup>C chemical shift of the aromatic carbons in *N,N*-dimethylaniline *N*-oxide [ $\delta$ (<sup>13</sup>C(CDCl<sub>3</sub> 50% v/v) C-1 = 154.6; C-2,6 = 120.0; C-3,5 = 129.0; C-4 = 128.8 and C-7 = 63.5 ppm].<sup>c</sup> Values in parentheses are for the other rotamer of **3c**.

u Indicates unresolved signal.

**Table 4. Carbon-13 chemical shift assignments relative to TMS for *N*-(2-nitrophenyl)amine *N*-oxides (4)<sup>a</sup>**

| Compound No.       | C-1                | C-2                | C-3                  | C-4   | C-5     | C-6     | C-7    | C-8    | C-9    | C-10   | C-11   | C-12   |
|--------------------|--------------------|--------------------|----------------------|-------|---------|---------|--------|--------|--------|--------|--------|--------|
| <b>4a</b>          | 147.0              | 145.0              | 125.4                | 130.4 | 131.4   | 122.2   | 63.0   | —      | —      | —      | —      | —      |
| Calc. <sup>b</sup> | 149.8              | 140.0              | 124.2                | 129.7 | 134.8   | 120.9   |        |        |        |        |        |        |
| <b>4b</b>          | 148.3              | 145.4              | 124.9                | 129.9 | 130.6   | 122.2   | 67.9   | 20.5   | 20.8   | 20.5   | 67.9   | —      |
| <b>4c</b>          | 148.8 <sup>c</sup> | 147.9 <sup>c</sup> | 125.4                | 129.8 | 130.4   | 122.0   | 71.3   | 28.3   | 22.4   | 20.9   | 61.3   | 15.5   |
|                    |                    |                    | (125.8) <sup>d</sup> | (u)   | (u)     | (122.7) | (71.7) | (26.3) | (u)    | (20.6) | (u)    | (16.1) |
| <b>4d</b>          | 147.7              | 145.7              | 125.2                | 129.8 | 130.6   | 121.1   | 74.4   | 26.4   | 30.4   | 20.7   | 68.1   | 18.3   |
|                    |                    |                    | (125.5)              | (u)   | (130.3) | (u)     | (73.9) | (28.4) | (29.3) | (19.8) | (69.9) | (19.3) |
| <b>4e</b>          | 147.0              | 145.8              | 125.3                | 130.2 | 131.0   | 121.4   | 68.4   | 28.9   | 28.8   | 28.9   | 68.4   | 21.8   |
| <b>4f</b>          | 147.0              | 145.4              | 125.1                | 130.3 | 131.0   | 122.0   | 67.0   | 61.2   | —      | 61.2   | 67.0   | —      |

<sup>a</sup> The numbering of the carbon atoms corresponds with that in Scheme 1.<sup>b</sup> See Table 3, footnote b.<sup>c</sup> These assignments can be reversed.<sup>d</sup> The values in parentheses are for the other rotamers of **4c** and **4d**.

u Indicates unresolved signal.

**Table 5. Carbon-13 chemical shift assignments relative to TMS for *O*-(4-nitrophenyl)hydroxylamines (5)<sup>a</sup>**

| Compound No. | C-1   | C-2   | C-3   | C-4   | C-5   | C-6   | C-7  | C-8  | C-9  | C-10 | C-11 | C-12 |
|--------------|-------|-------|-------|-------|-------|-------|------|------|------|------|------|------|
| <b>5b</b>    | 164.6 | 113.8 | 125.8 | 141.5 | 125.8 | 113.8 | 56.9 | 25.4 | 23.3 | 25.4 | 56.9 | —    |
| <b>5c</b>    | 165.9 | 114.1 | 125.8 | 141.8 | 125.8 | 114.1 | 62.6 | 34.2 | 23.8 | 25.7 | 56.7 | 19.6 |
| <b>5d</b>    | 164.6 | 113.8 | 125.8 | 141.7 | 125.8 | 113.8 | 67.2 | 31.8 | 31.8 | 24.9 | 64.0 | 19.3 |
| <b>5e</b>    | 164.6 | 113.9 | 125.8 | 141.6 | 125.8 | 113.8 | 56.5 | 33.9 | 30.0 | 33.9 | 56.5 | 21.2 |
| <b>5f</b>    | 163.9 | 113.8 | 126.0 | 135.5 | 126.0 | 113.8 | 56.3 | 66.0 | —    | 66.0 | 56.3 | —    |

<sup>a</sup> The numbering of the carbon atoms corresponds with that in Scheme 1.**Table 6. Carbon-13 chemical shift assignments relative to TMS for *O*-(2-nitrophenyl)hydroxylamine (6)<sup>a</sup>**

| Compound No. | C-1   | C-2   | C-3   | C-4   | C-5   | C-6   | C-7  | C-8  | C-9  | C-10 | C-11 | C-12 |
|--------------|-------|-------|-------|-------|-------|-------|------|------|------|------|------|------|
| <b>6b</b>    | 153.3 | 138.7 | 125.4 | 120.4 | 134.3 | 116.7 | 56.9 | 25.3 | 23.3 | 25.3 | 56.9 | —    |
| <b>6c</b>    | 154.4 | 137.7 | 125.4 | 120.0 | 134.2 | 116.8 | 62.6 | 34.2 | 23.8 | 25.9 | 56.9 | 19.8 |
| <b>6d</b>    | 153.2 | 137.7 | 125.8 | 120.4 | 134.4 | 116.7 | 64.1 | 31.8 | 31.8 | 24.9 | 56.3 | 19.4 |
| <b>6e</b>    | 153.3 | 137.8 | 125.4 | 120.4 | 134.4 | 116.4 | 56.5 | 34.0 | 30.0 | 34.0 | 56.5 | 21.2 |

<sup>a</sup> The numbering of the carbon atoms corresponds with that in Scheme 1.

reported values for *p*-nitroaniline.<sup>12</sup> The good agreement between the calculated and the observed values for **1a** and **1f** (Table 1) supports the above analysis. The calculated values were obtained using the  $-\text{NO}_2$  effect<sup>13</sup> on the aromatic  $^{13}\text{C}$  chemical shift of *N,N*-dimethylaniline<sup>14</sup> and *N*-arylmorpholine, respectively.<sup>15</sup>

Inspection of the  $^{13}\text{C}$  NMR spectra of **1a–1f**, all obtained using the same acquisition parameters, showed that the signals for the carbon bearing the nitro group are broader than that bearing the amine moiety, and this could be due to the Overhauser effect of the methyl (**1a**) or the methylene (**1b–1f**) groups connected to the nitrogen atom.

(b) *N*-(2-Nitrophenyl)amines **2a–2f**: the analysis of the  $^{13}\text{C}$  chemical shifts for the aromatic ring carbons in **2a–2f** (Table 2) was carried out using the  $^{13}\text{C}$  chemical shift values for *o*-nitroaniline.<sup>16</sup> The agreement between the calculated and observed values for **2a** and **2f** supports the above assignment, except for C-2 where the discrepancy between the calculated and observed values could be attributed to steric interaction (induced shift).<sup>17</sup>

#### *N*-Aryl-*tert*-amine oxides 3 and 4.

(a) *N*-(4-Nitrophenyl)amine *N*-oxides **3a–3f**: the  $^{13}\text{C}$  NMR spectral assignments, carried out from the calculated shifts of **3a**, are reported in Table 3.

(b) *N*-(2-nitrophenyl)amine *N*-oxides **4a–4f**: the broad band  $^{13}\text{C}$  NMR spectra of **4a–4f** are reported in Table 4. The calculated  $^{13}\text{C}$  signals for *N,N*-dimethylaniline *N*-oxide were used to confirm the spectral analysis for **4a**. The difference between the calculated and observed  $^{13}\text{C}$  chemical shift for C-2 in **4a** (~5 ppm) may be due to a steric effect.<sup>17</sup>

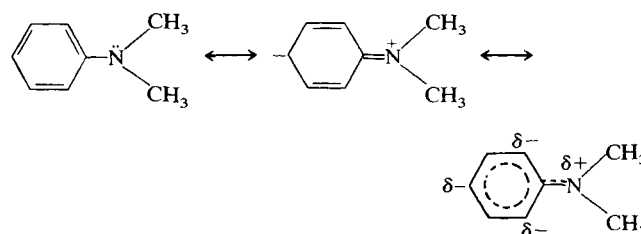
***O*-Arylhydroxylamines 5 and 6.** The proton decoupled  $^{13}\text{C}$  spectra of **5** and **6** are reported in Tables 5 and 6, respectively. The assignments of the  $^{13}\text{C}$  chemical shifts for the aryl carbon atoms in the 4-nitrophenylhydroxylamines **5b–5f** and 2-nitrophenylhydroxylamines **6b–6f** were made by using the reported  $^{13}\text{C}$  chemical shift for *p*-nitro-<sup>18</sup> and *o*-nitrophenol, respectively.

## DISCUSSION

### The *N*-oxidation effect

#### The *N*-oxidation effect for the $^{13}\text{C}$ chemical shifts of *N*-(4-nitrophenyl)amine *N*-oxides (**3a–3f**).

(a) *N*-oxidation effect on the aromatic ring: the substitution of one hydrogen in benzene by the *N,N*-dimethylamine group induces an upfield shift for the *o*- and *p*-carbons of  $-16$  and  $-12$  ppm, respectively. This has been attributed to the mesomeric effect, in which the paired electrons of the nitrogen are used up in the resonance.<sup>19</sup>



This resonance is interrupted by *N*-oxidation of the molecule, and so a deshielding is expected for the *ortho*- and *para*-carbons. Indeed, C-2 and C-4 are deshielded by  $+7.3$  and  $+12.8$  ppm, respectively, C-1 experiences a deshielding of  $+3.9$  ppm and C-3,5 show no effect (Tables 1 and 3). Table 7 shows a similar pattern for the *N*-oxide effect on the *p*-nitrophenyl group in **3a–3f**.

(b) The *N*-oxidation effect on the aliphatic carbon atoms: a downfield shift in the range of  $+17.5$  to  $+24.5$  ppm is observed for the ring carbons C-7 and C-11 ( $\beta$ -effect) due to *N*-oxidation (Table 7). Shielding is observed for the ring C-8 and C-10 carbons ( $-3.5$  to  $-4.6$  ppm;  $\gamma$ -effect) and for C-9 ( $-1.6$  to  $2.3$  ppm;  $\delta$ -effect).

#### The *N*-oxidation effect for the *N*-(2-nitrophenyl)amines (**4a–4f**).

(a) *N*-oxidation effect on the aromatic ring: the *N*-oxidation effect for **4a–4f** is indicated in Table 8.

**Table 7. N-oxidation effect on the <sup>13</sup>C chemical shift of N-(4-nitrophenyl)amines (1)<sup>a</sup>**

| Compounds    | ΔδC-1 | ΔδC-2 | ΔδC-3 | ΔδC-4 | ΔδC-5 | ΔδC-6 | ΔδC-7 | ΔδC-8 | ΔδC-9 | ΔδC-10 | ΔδC-11 | ΔδC-12 |
|--------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|--------|--------|
| <b>3a-1a</b> | +3.8  | +11.6 | -1.1  | +10.4 | -1.1  | +11.6 | +22.4 | —     | —     | —      | —      | —      |
| <b>3b-1b</b> | +6.1  | +10.1 | -1.5  | +10.1 | -1.5  | +10.1 | +20.8 | -4.1  | -2.3  | -4.1   | +20.8  | —      |
| <b>3c-1c</b> | +4.5  | +10.4 | -1.9  | +9.8  | -1.9  | +10.4 | +24.5 | -4.1  | -2.2  | -4.6   | +17.5  | +1.4   |
| <b>3d-1d</b> | +5.9  | +10.0 | -1.6  | +10.3 | -1.6  | +10.0 | +20.0 | -3.8  | -2.3  | -3.5   | +20.8  | -0.5   |
| <b>3e-1e</b> | +6.2  | +9.9  | -1.6  | +10.4 | -1.6  | +9.9  | +21.3 | -4.1  | -1.6  | -4.1   | +21.3  | -0.2   |
| <b>3f-1f</b> | +4.5  | +9.6  | -1.0  | +8.1  | -1.0  | +9.6  | +20.8 | -4.2  | —     | -4.2   | +20.8  | —      |

<sup>a</sup> ΔδC = δC of the N-oxide (3) - δC of the corresponding amine (1).

**Table 8. N-oxidation effect on the <sup>13</sup>C chemical shift of N-(2-nitrophenyl)amines(2)<sup>a</sup>**

| Compounds    | ΔδC-1 | ΔδC-2 | ΔδC-3 | ΔδC-4 | ΔδC-5 | ΔδC-6 | ΔδC-7 | ΔδC-8 | ΔδC-9 | ΔδC-10 | ΔδC-11 | ΔδC-12 |
|--------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--------|--------|--------|
| <b>4a-2a</b> | +0.8  | +5.5  | -1.1  | +12.1 | -1.8  | +5.3  | +20.7 | —     | —     | —      | —      | —      |
| <b>4b-2b</b> | +1.2  | +2.9  | -0.9  | +8.6  | -2.6  | +1.4  | +14.7 | -5.6  | -3.3  | -5.6   | +14.3  | —      |
| <b>4c-2c</b> | +3.0  | +0.2  | +0.4  | +5.8  | -1.8  | -1.5  | +16.3 | -5.2  | +0.2  | -5.6   | 8.3    | -2.8   |
| <b>4d-2d</b> | +0.8  | +3.0  | -0.5  | +8.8  | -2.8  | +0.6  | +14.7 | -4.7  | -2.2  | -4.8   | +15.5  | -0.8   |
| <b>4e-2e</b> | 0     | +3.1  | -0.7  | +9.2  | -2.4  | +0.8  | +16.2 | -5.4  | -1.8  | -5.4   | 16.2   | 0      |
| <b>4f-2f</b> | +0.8  | +0.6  | +0.7  | +7.8  | -2.5  | +0.7  | 14.7  | -5.7  | —     | -5.7   | 14.7   | —      |

<sup>a</sup>ΔδC = δC of the N-oxide (4) - δC of the corresponding amine (2).

**Table 9. N-oxidation effect on the <sup>13</sup>C chemical shift of 3-nitro-N,N-dimethylaniline**

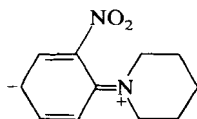
|                      | C-1   | C-2   | C-3   | C-4   | C-5   | C-6   | C-7  |
|----------------------|-------|-------|-------|-------|-------|-------|------|
| Amine <sup>a</sup>   | 150.8 | 106.0 | 149.4 | 110.5 | 129.5 | 117.6 | 40.1 |
| N-oxide <sup>b</sup> | 153.3 | 116.0 | 148.8 | 124.8 | 131.1 | 131.1 | 62.2 |
| N-oxide effect       | +2.5  | +10   | -0.8  | +14.3 | +1.6  | 13.5  | 12.1 |

<sup>a</sup> The assignment of 3-nitro-N,N-dimethylaniline was achieved using the reported value of *m*-nitroaniline.<sup>1</sup>

<sup>b</sup> The assignment of the N-oxide was achieved using the -NO<sub>2</sub> effect on the <sup>13</sup>C chemical shifts of N,N-dimethylaniline N-oxide.

Compound **4a** showed a similar pattern on N-oxidation as N,N-dimethylaniline. The effect of N-oxidation on the aromatic ring in **4b-4f** showed a similar pattern for C-1, C-3 and C-5 to that of the corresponding carbons in **4a**. However, the effect on C-2 and C-6 (*ortho* effect) and C-4 (*para* effect) is much smaller than in **4a**, although in the same direction. This could be due to steric interaction between the neighbouring NO<sub>2</sub> group and the heterocyclic ring in the amine. This prevents the conjugated system from attaining coplanarity, thereby reducing the electronic interaction between the aromatic π-system and

the N lone pair of electrons, and canonical forms such as



are, thus, less important than in the *p*- and *m*-NO<sub>2</sub> aromatic compounds. Accordingly, **4b-4f** did not show the true N-oxidation effect seen with **4a** or with the *p*-nitro compounds (**3a-3f**) and 3-nitro-N,N-dimethylaniline (see Table 9). Support for the above argument is given by the <sup>13</sup>C chemical shift values of **2c** in which a methyl group is present in the heterocyclic ring at the 2-position, making steric crowding in this compound even more severe than in the other isomers. C-2, C-4 and C-6 are more deshielded in **2c** than in the other congeners (Table 2).

Dreiding models of **2c** and **4c** show clearly that the

*o*-nitrophenyl group is not coplanar with the heterocyclic ring, but is nearly perpendicular due to the steric hindrance to rotation. It is of interest to note the appearance of two <sup>13</sup>C signals for some of the aromatic and heterocyclic ring carbon atoms in **4c** (Table 4), thus suggesting the possibility of the existence of two rotational isomers. The same phenomenon is noted in **3c** and **4d**.

(b) The N-oxidation effect on the aliphatic carbon atoms: it is clear from Tables 7 and 8 that the N-oxidation effect on the N-methyl carbon atoms in **4a** has a similar value as in the *p*-nitro isomer **3a**. However, in **4b-4f**, the N-oxidation effect on the N-CH<sub>2</sub> carbon atoms (C-7 and C-11) has a smaller value than for the N-CH<sub>3</sub> carbon in **4a**. The difference is due to the steric effect induced by the presence of the -NO<sub>2</sub> group in the *ortho*-position, positioning the N-CH<sub>2</sub> carbon out of the electrical field effect of the aromatic ring. Indeed, the situation becomes more severe in compound **4c**, which has a methyl group at C-7.

## EXPERIMENTAL

### Synthesis

The tertiary amines were synthesized by nucleophilic substitution of the appropriate secondary amines with *o*-nitro- and *p*-nitro-fluorobenzene in dimethyl sulphoxide.<sup>9,20</sup> The N-oxides were prepared by oxidation

of the tertiary amines with performic acid (a mixture of 98% formic acid and 30% hydrogen peroxide).<sup>9,21</sup> Rearrangement of the tertiary amine *N*-oxides was performed by heating the free base in dioxane for 3 h.<sup>9</sup> The products were purified by column chromatography with neutral alumina. The preparative details of these compounds are reported in Ref. 9.

### Carbon-13 NMR spectra

Proton decoupled and coupled spectra were obtained

on a Bruker WH 90 DS spectrometer equipped with an Aspect 2000, 32 K computer, operating at 22.63 MHz for <sup>13</sup>C NMR with internal deuterium lock. The spectral width was 6024 Hz; a flip angle of 45° was used and the free induction decay was accumulated in 8 K, and the frequency domain spectra obtained in 4 K, data points. Samples were dissolved in CDCl<sub>3</sub> 10–15% by v/v or w/v in a 10 mm o.d. Wilmad tube, and a few drops of TMS were added as internal reference.

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