Colour and Constitution of 1,4-Naphthoquinonoid Dyes – Modified PPP MO Calculations and Substituent Effects

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Calculation of the \( \pi \)-electron excitation energies of naphthoquinonoid dyes has been carried out by means of the Pariser—Parry—Pople (PPP) method using the variable, \( \beta \)+y approximation. A good linear correlation between the observed and calculated values for the first \( \pi-\pi^* \) excitation was found for a new series of naphthoquinonoid dyes. The effect of substituents on the colour of different dyes was studied on the basis of these calculated results, i.e. HOMO—LUMO energy levels and \( \pi \)-electron-density changes accompanying the excitation. The intramolecular charge-transfer character of the \( \pi-\pi^* \) transition was shown to be the same as occurs in some anthraquinonoid dyes.

INTRODUCTION
Analyses of the colour and constitution properties of quinonoid dyes by means of the PPP molecular orbital (MO) method has been summarised by Griffiths [1], and Fabian and Hartmann [2]. We have also studied substituent and annelation effects in anthraquinonoid dyes by means of a modified PPP MO method [3,4]. In the case of donor substituted 1,4-naphthoquinonoid dyes, Griffiths et al. [5–8] have recently reported electronic absorption spectra, and interpreted the spectra with the aid of PPP MO calculations. These results indicated that there are two overlapping \( \pi-\pi^* \) transitions, one involving electron-density migration from the benzenoid donor groups into the quinonoid system, and the other involving a similar transfer of negative charge from the quinonoid donor groups. In the present paper, the colour and constitution properties of a new series of naphthoquinonoid dyes were investigated using their absorption spectra and a modified PPP MO method, with the intention of correlating the substituent effects with the colour of the dyes.

EXPERIMENTAL AND CALCULATION
Dyes used were synthesised in our laboratory and were purified by chromatography over silica gel followed by repeated recrystallisation. The results of elementary analysis were consistent with the theoretical values. Methods of synthesis have been reported in the literature as follows: dyes 1 and 3 [9]; 4, 6, 7, 8, 14, 15 and 16 [10]; 9 [6]; 10 and 17 [7]; 11, 12, 13, 18, 19 and 20 [11]. Dye 2 was synthesised by the reaction of 2,3-dichloronaphthoquinone with sodium cyanide [12], m.p. 259–262°C (chloroform); n.m.r., \( \delta =8.0 \) (singlet); mass spectrum, M 208, M–28 180. Dye 5 has been synthesised and the experimental details reported [13].

UNLESS OTHERWISE STATED, absorption spectra were measured in benzene at the concentration of \( 1 \times 10^{-4} \) mol/l using a Hitachi EPS–3T recording spectrophotometer. The modified PPP MO calculations were carried out by the method described previously [3].

RESULTS AND DISCUSSION
Relationship between Calculated and Observed Values
The calculated results are summarised in Tables 1 and 2, together with the experimental \( \lambda_{\text{max}} \) values. It is well known that the visible absorption bands of 1,4-naphthoquinonoid dyes can be assigned to benzenoid and/or quinonoid bands of intramolecular charge-transfer character [5–8]. In Figure 1 the calculated first excitation energies \( (\Delta E) \) are plotted against the observed value \( (\Delta E_{\text{obs}}) \), which were obtained from the \( \lambda_{\text{max}} \) values in benzene. A good linear correlation between observed and calculated values for the first \( \pi-\pi^* \) excitation was found, summarised by Eqn 1.

\[
\Delta E_{\text{max}} \quad (\text{eV}) = 1.06 \times \Delta E_{\text{obs}} - 0.382
\]

A different linear plot with the same slope was also obtained from another series of 1,4-naphthoquinonoid dyes, which has been reported by Griffiths [6,7], summarised by Eqn 2.

\[
\Delta E_{\text{max}} \quad (\text{eV}) = 1.06 \times \Delta E_{\text{obs}} - 0.180
\]

The mismatch of the two lines can be attributed to the use of different values for the parameters in each of the MO calculations [3–8]. In both cases, the MO results for the first benzenoid excitation energy satisfactorily reproduce the character of the observed values. The value (1.06) of the slope of Eqn 1 was essentially the same as the value (1.056) for anthraquinonoid dyes which had been previously reported [3]. This indicates that both types of quinonoid dye show the same intramolecular charge-transfer character for the first benzenoid transition. On the other hand, the agreement between calculated and observed values for the second (quinonoid) band is less satisfactory, but the calculated results qualitatively reproduce relative trends in the observed \( \lambda_{\text{max}} \) values (Table 2).

Benzenoid Transition
A good linear correlation exists between the first excitation energy, \( \Delta E_{\text{obs}} \), and the singly excited configuration energy \( (\varepsilon_{\text{1s}}-\varepsilon_{\text{2s}}) \) accompanying the excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) (correlation coefficient 0.986). This shows that the first excitation energy depends markedly on the character of the HOMO and LUMO. In the following section substituent effects on the benzenoid bands are discussed in terms of the first excitation energy \( (\Delta E_{\text{obs}}) \) and the energy levels of the HOMO and LUMO. In the
### TABLE 1

#### Summary of Results for the Benzenoid Band

<table>
<thead>
<tr>
<th>Dye No.</th>
<th>Substituent&lt;sup&gt;(a)&lt;/sup&gt;</th>
<th>ε&lt;sub&gt;HOMO&lt;/sub&gt;&lt;sup&gt;(b)&lt;/sup&gt; (eV)</th>
<th>ε&lt;sub&gt;LUMO&lt;/sub&gt;&lt;sup&gt;(c)&lt;/sup&gt; (eV)</th>
<th>Δε&lt;sup&gt;(d)&lt;/sup&gt; (eV)</th>
<th>f&lt;sup&gt;(e)&lt;/sup&gt;</th>
<th>Δε&lt;sub&gt;max&lt;/sub&gt; (eV)</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt;&lt;sup&gt;(f)&lt;/sup&gt; (nm)</th>
<th>ε&lt;sub&gt;max&lt;/sub&gt; (×10&lt;sup&gt;-4&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2,3-di-CN</td>
<td>10.521</td>
<td>3.636</td>
<td>3.732</td>
<td>0.111</td>
<td>3.70</td>
<td>335&lt;sup&gt;(g)&lt;/sup&gt;</td>
<td>0.30&lt;sup&gt;(g)&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>5,8-di OH</td>
<td>10.785</td>
<td>4.484</td>
<td>3.487</td>
<td>0.113</td>
<td>3.40</td>
<td>365</td>
<td>0.39</td>
</tr>
<tr>
<td>3</td>
<td>5,8-di OH-2 NH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>9.049</td>
<td>3.412</td>
<td>2.735</td>
<td>0.254</td>
<td>2.89</td>
<td>429&lt;sup&gt;(g)&lt;/sup&gt;</td>
<td>0.36&lt;sup&gt;(g)&lt;/sup&gt;</td>
</tr>
<tr>
<td>4</td>
<td>5,8-di OH-2-NHR</td>
<td>8.921&lt;sup&gt;(h)&lt;/sup&gt;</td>
<td>3.078</td>
<td>2.919&lt;sup&gt;(i)&lt;/sup&gt;</td>
<td>0.138</td>
<td>2.48</td>
<td>500</td>
<td>0.69</td>
</tr>
<tr>
<td>5</td>
<td>5,6,8-di OH-6,7-di NHR</td>
<td>9.384&lt;sup&gt;(h)&lt;/sup&gt;</td>
<td>2.947</td>
<td>2.613&lt;sup&gt;(i)&lt;/sup&gt;</td>
<td>0.236</td>
<td>2.48</td>
<td>501</td>
<td>1.18</td>
</tr>
<tr>
<td>6</td>
<td>5-OH-6,7,8-tri NHR</td>
<td>7.767</td>
<td>2.814</td>
<td>2.385</td>
<td>0.293</td>
<td>2.37</td>
<td>523</td>
<td>1.57</td>
</tr>
<tr>
<td>7</td>
<td>5-NH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>9.184</td>
<td>3.466</td>
<td>2.761</td>
<td>0.184</td>
<td>2.56</td>
<td>484&lt;sup&gt;(i)&lt;/sup&gt;</td>
<td>0.54&lt;sup&gt;(i)&lt;/sup&gt;</td>
</tr>
<tr>
<td>8</td>
<td>5-NH&lt;sub&gt;2&lt;/sub&gt;-2,3-di CN</td>
<td>9.445</td>
<td>4.332</td>
<td>2.438</td>
<td>0.171</td>
<td>2.12</td>
<td>585</td>
<td>0.41</td>
</tr>
<tr>
<td>9</td>
<td>5-NH&lt;sub&gt;2&lt;/sub&gt;-2-CN-3-NHR</td>
<td>9.276</td>
<td>3.515</td>
<td>2.787</td>
<td>0.196</td>
<td>2.56</td>
<td>484</td>
<td>0.56</td>
</tr>
<tr>
<td>10</td>
<td>5-NH&lt;sub&gt;2&lt;/sub&gt;-2-CN-3-NHR</td>
<td>9.092</td>
<td>3.548</td>
<td>2.663</td>
<td>0.164</td>
<td>2.44</td>
<td>509</td>
<td>0.52</td>
</tr>
<tr>
<td>11</td>
<td>5-NH&lt;sub&gt;2&lt;/sub&gt;-2-CN-3-NHR</td>
<td>8.732</td>
<td>3.405</td>
<td>2.548</td>
<td>0.294</td>
<td>2.30</td>
<td>540</td>
<td>0.94</td>
</tr>
<tr>
<td>12</td>
<td>5,8-di NHR</td>
<td>7.962</td>
<td>3.126</td>
<td>2.233</td>
<td>0.331</td>
<td>1.94</td>
<td>638</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>5,8,9-tri NHR</td>
<td>7.736</td>
<td>2.812</td>
<td>2.275</td>
<td>0.338</td>
<td>2.07</td>
<td>598</td>
<td>1.60</td>
</tr>
<tr>
<td>14</td>
<td>5,8,9-tri NHR</td>
<td>7.668</td>
<td>2.849</td>
<td>2.269</td>
<td>0.372</td>
<td>2.02</td>
<td>614</td>
<td>1.13</td>
</tr>
<tr>
<td>15</td>
<td>5-NH&lt;sub&gt;2&lt;/sub&gt;-2-CN-3-NHR</td>
<td>8.503</td>
<td>4.076</td>
<td>1.992</td>
<td>0.300</td>
<td>1.69</td>
<td>735</td>
<td>0.86</td>
</tr>
<tr>
<td>16</td>
<td>5,8,9-tri NHR</td>
<td>8.143</td>
<td>3.282</td>
<td>2.235</td>
<td>0.310</td>
<td>2.03</td>
<td>612</td>
<td>1.15</td>
</tr>
<tr>
<td>17</td>
<td>5-NH&lt;sub&gt;2&lt;/sub&gt;-2,NHPh-2,3-di CN</td>
<td>8.236</td>
<td>3.282</td>
<td>2.317</td>
<td>0.331</td>
<td>2.06</td>
<td>603</td>
<td>1.10</td>
</tr>
<tr>
<td>18</td>
<td>5-NH&lt;sub&gt;2&lt;/sub&gt;-2,NHPh-2,3-di CN</td>
<td>8.188</td>
<td>3.293</td>
<td>2.257</td>
<td>0.307</td>
<td>2.05</td>
<td>605</td>
<td>1.10</td>
</tr>
</tbody>
</table>

<sup>(a)</sup> R = 1-butyl  
<sup>(b)</sup> Energy of the highest occupied molecular orbital (HOMO)  
<sup>(c)</sup> Energy of the lowest unoccupied molecular orbital (LUMO)  
<sup>(d)</sup> First excitation energy  
<sup>(e)</sup> Oscillator strength for the benzenoid transition  
<sup>(f)</sup> λ<sub>max</sub> denotes the position of the central peak of three peaks in the first visible absorption band  
<sup>(g)</sup> Measured in chloroform [9]  
<sup>(h)</sup> Energy of the next highest occupied molecular orbital (NHOMO)  
<sup>(i)</sup> Second excitation energy  
<sup>(j)</sup> Measured in cyclohexane [6]

### TABLE 2

#### Summary of Results for the Quinonoid Band

<table>
<thead>
<tr>
<th>Dye No.</th>
<th>Substituent&lt;sup&gt;(a)&lt;/sup&gt;</th>
<th>ε&lt;sub&gt;HOMO&lt;/sub&gt;&lt;sup&gt;(a)&lt;/sup&gt; (eV)</th>
<th>ε&lt;sub&gt;LUMO&lt;/sub&gt;&lt;sup&gt;(b)&lt;/sup&gt; (eV)</th>
<th>Δε&lt;sup&gt;(c)&lt;/sup&gt; (eV)</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt;&lt;sup&gt;(d)&lt;/sup&gt; (nm)</th>
<th>f&lt;sup&gt;(e)&lt;/sup&gt;</th>
<th>ε&lt;sub&gt;max&lt;/sub&gt; (×10&lt;sup&gt;-4&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>2-NH&lt;sub&gt;2&lt;/sub&gt;-5,8-di OH</td>
<td>9.236</td>
<td>3.146</td>
<td>3.025</td>
<td>410</td>
<td>0.083</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2-NHR-5,8-di OH</td>
<td>8.814&lt;sup&gt;(g)&lt;/sup&gt;</td>
<td>3.078</td>
<td>2.780&lt;sup&gt;(h)&lt;/sup&gt;</td>
<td>446</td>
<td>0.234</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>5-NHR-2-CN-3-NHR</td>
<td>9.316</td>
<td>3.515</td>
<td>3.057</td>
<td>405</td>
<td>0.176</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>5-NH&lt;sub&gt;2&lt;/sub&gt;-2-CN-3-NHR</td>
<td>9.207</td>
<td>3.405</td>
<td>2.988</td>
<td>414</td>
<td>0.130</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>5-NH&lt;sub&gt;2&lt;/sub&gt;-2-CN-3-NHR</td>
<td>9.087</td>
<td>3.282</td>
<td>2.975</td>
<td>417</td>
<td>0.124</td>
<td></td>
</tr>
</tbody>
</table>

<sup>(a)</sup> Energy of the next highest occupied molecular orbital (NHOMO)  
<sup>(b)</sup> Energy of the lowest unoccupied molecular orbital (LUMO)  
<sup>(c)</sup> Second excitation energy  
<sup>(d)</sup> Calculated from Δε<sub> max</sub> value  
<sup>(e)</sup> A broad peak caused confusion in the estimation of the observed λ<sub>max</sub> value  
<sup>(f)</sup> No detectable shoulder  
<sup>(g)</sup> Energy of the highest occupied molecular orbital (HOMO)  
<sup>(h)</sup> First excitation energy

---

From the results, the following observations were made:

1. Substitution of the strong acceptor group (CN) in the 2- and 3-positions causes a small decrease in ε<sub>HOMO</sub> and a large decrease in ε<sub>LUMO</sub>, i.e. increasing the power of an acceptor in the intramolecular charge-transfer transition produces a bathochromic shift of the benzenoid band.

2. Substitution of a strong donor group (e.g. NH or NHPh) in the 5- and/or 8-positions causes a large increase in
Figure 1 – Relationship between the calculated excitation energy (ΔE,) and the observed value (ΔE_max) for the benzenoid band (for numbering system see Table 1).

Figure 2 – Substituent effects on ε_HOMO, ε_HOMO, and ε_LUMO for (A) benzenoid and (B) quinonoid transitions (for numbering system see Table 1).

ε_HOMO and a small increase in ε_LUMO, i.e. increasing the power of the donor group produces a large bathochromic shift.

3. Substitution of a donor group in the 2- or 3-position causes a small increase in ε_HOMO and a large increase in ε_LUMO, producing a hypsochromic shift.

From these results it was apparent that the donor-substituted benzenoid moiety played a role as donor and the quinonoid moiety played a role as acceptor. The intramolecular charge-transfer character of the benzenoid band was confirmed as being the same as in the case of the donor-substituted anthraquinone series [3,4].

Quinonoid Transition

The quinonoid bands of naphthoquinonoid dyes were generally observed in the range 400–500 nm, appearing as broad bands which sometimes confused estimation of the λ_max values. The MO calculations revealed that the quinonoid band of dyes studied was attributable to the second \( \pi^* \) transition from the next highest occupied MO (NHOMO) to LUMO except in the case of dye 6. The results are summarised in Figure 2 and Table 2. Substituent effects on the quinonoid bands were rather small in comparison with those on benzenoid bands, i.e. replacement of a hydroxy group in dye 13 by a butylamino group as in 18 produces a 10 nm hypsochromic shift of the quinonoid band, but a 72 nm bathochromic shift of the benzenoid band. The calculated values were in the range from 400 to 450 nm, while the observed values were about 450 nm. It was found that the quinonoid band was not affected significantly by benzenoid donor substituents, as shown by comparison of 11 with 13, and 13 with 18.

From the \( \pi \)-electron-density changes accompanying the quinonoid transition, it was found that the quinonoid donor substituent (2- or 3-NHR) played a role as electron donor and the 1,4-benzoquinone moiety acted as acceptor; 5,8-donor substituents had little effect on the quinonoid band. It was also found that the substituent effects for the quinonoid band on \( \epsilon_{\text{NHOMO}} \) and \( \epsilon_{\text{LUMO}} \) were rather smaller than those for the benzenoid band (Figure 2).

\( \pi \)-Electron-density Changes Accompanying the Transition

Typical \( \pi \)-electron-density changes accompanying the benzenoid and quinonoid transitions of naphthoquinonoid dyes have been calculated and reported by Griffiths et al. [5-8]. They found that in the case of, for example, 5-amino-3-methylamino-1,4-naphthoquinone, the calculated electron-density changes for the first benzenoid band showed a pronounced migration of electron density from the 5-amino group into the quinonoid ring, whereas the 3-methylamino group was virtually unaffected. In this respect the pattern is analogous to that found for the visible band of 5-amino-1,4-naphthoquinone. On the other hand, electron-density changes for the second benzenoid band showed that the 3-methylamino group transferred a significant amount of negative charge to the quinonoid ring, and the 5-amino group virtually no part in the transition. The situation parallels that found for 2-methylamino-1,4-naphthoquinone. Thus, in this case, it is reasonable to assign the two bands of 5-amino-3-methylamino-1,4-naphthoquinone to the visible transitions shown separately by the two parent molecules.

We obtained similar results for dyes 11–13, 15 and 18–20 (Figure 3). However, in the case of dyes 5 and 6 the situation was quite different and the charge migrations were more complicated (Figure 3), i.e. the first transition in dye 6 was...
quionoid in character, and the second one was benzenoid in character, while the reverse was true for dye 5. In dyes 5 and 6 the negative charge migrated from each of the donor substituents to the quinone ring. In the case of dye 6 a larger amount of negative charge migrated from the 2-butylamino group than from the 5,8-hydroxyl groups in the first quinoid transition, while in the second benzenoid transition the opposite was found. Thus, both the quinonoid 2-butylamino group and the benzenoid 5,8-hydroxyl groups had a strong influence on the two transitions. The effects of quinonoid substituents on the benzenoid transition the opposite was found. Thus, both the 2-butylamino group than from the 5,8-hydroxyl groups in larger amount of negative charge migrated from the donor substituents was completely neglected. With dyes 7 and 8 the donor properties of 6,7-butylamino groups were largely overestimated, and consequently the calculated charge migration for the first and the second transitions were anomalous (Figure 5). It may be necessary to take into account the steric effects of substituents.

SCOPE AND LIMITATION

It was found that the PPP MO method can quantitatively reproduce the absorption spectra of naphthoquinonoid dyes, as has been found for anthraquinonoid dyes [3,4]. The absorption spectra could be interpreted in terms of the calculated values of $\epsilon_{\text{HOMO}}$, $\epsilon_{\text{NHOMO}}$ and $\epsilon_{\text{LUMO}}$, and the $\pi$-electron-density changes. Substituent effects on the benzenoid band could be correlated with Eqn 1, but a similar attempted correlation with the quinonoid band was unsuccessful. There are some effects that could not be interpreted by the PPP MO calculations procedure used, as outlined below.

1. Dyes 5, 6, 7 and 8 deviated from the line (Figure 1). With dyes 5 and 6 both the benzenoid and quinonoid bands closely overlapped (Tables 1 and 2). The quinonoid 2-amino group (strong donor) and the benzenoid 5,8-hydroxyl groups (weak donors) strongly influenced each other, and, exceptionally, negative charges migrated from each of the donor substituents to the quinoid ring accompanying the transition (Figure 3).

Calculations were carried out assuming a planar geometry; the steric repulsion of each benzenoid substituents was completely neglected. With dyes 7 and 8 the donor properties of 6,7-butylamino groups were largely overestimated, and consequently the calculated charge migration for the first and the second transitions were anomalous (Figure 5). It may be necessary to take into account the steric effects of substituents.

**REFERENCES**

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