Nuclear Magnetic Resonance Studies on Aromatic Compounds, IV  
$^{13}$C NMR Spectra of Some Disulpho-substituted 1- and 2-Naphthols

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$^{13}$C NMR, 1-Naphthols, 2-Naphthols

The $^{13}$C NMR spectra of 1-hydroxynaphthalene-3,6-disulphonic, 1-hydroxynaphthalene-3,8-disulphonic, 2-hydroxynaphthalene-3,6-disulphonic, and 2-hydroxynaphthalene-6,8-disulphonic acids were determined with and without noise-decoupling. The fine splitting caused by the long-range couplings pattern was used in the identification of the resonances lines of the $^{13}$C nuclei. The combined influence of the mesomeric effect of the hydroxyl group and that of the sulphonate groups have been discussed.

The $^{13}$C NMR spectra of the following dihydroxy-naphthalenesulphonic acids were discussed in part III of this series: 1. 2,3-dihydroxynaphthalene-6-sulphonic acid (abbreviated as 236DHNS), chromotropic acid, and catechol-3,5-disulphonic acid (Tiron). In these three compounds we have analyzed the contribution of the mesomeric effect of the hydroxyl group. In the present work we have continued our investigations about aromatic sulpho-substituted compounds with four different naphthalenedisulphonic acids, each containing one hydroxyl group. The $^{13}$C NMR spectra of 1-hydroxynaphthalene-3,6-disulphonic (abbreviated here as 136HND$_S$), 1-hydroxynaphthalene-3,8-disulphonic (138HND$_S$), 2-hydroxynaphthalene-3,6-disulphonic (236HND$_S$), and 2-hydroxynaphthalene-6,8-disulphonic (268HND$_N$) acid were recorded and discussed.

Experimental

Reagents: All the naphtholsulphonates studied were reagents from either E. Merck AG or Fluka AG, and they were recrystallized several times from hot water before use.

Apparatus and methods: The $^{13}$C NMR spectra of the present compounds were determined from 20% solutions with Jeol's JNM–FX100 FT-spectrometer (in DQD mode and at 25.06 MHz) both with and without proton noise-decoupling. For all the spectra, the respective settings were the same as those reported in part I of this series. All the measurements were carried out in D$_2$O solution at 298 K with TMS as an external standard for chemical shifts. No corrections were made in the chemical shifts for the differences in bulk susceptibility, because all the molecules studied had the same solvent.

Results and Discussion

In this work we investigated the contribution of the hydroxyl and sulphonate groups to the distribution of $\pi$-electrons around the carbon nuclei in different disulphosubstituted 1- and 2-naphthols with aid of the changes in chemical shifts related to naphthalene measured from $^{13}$C NMR spectra. Our interest was particularly focussed on the mesomeric effect of these groups. The hydroxyl group has a positive mesomeric effect and a negative inductive effect. The inductive effect of the sulphonate group is parallel, to that of the hydroxyl group, whereas the mesomeric effect is reverse. All the other of these effects are relatively small, except the mesomeric effect of the hydroxyl group.

In all the sulphonate compounds studied in this series, the relatively large positive chemical shifts in the resonance lines of the carbons bonded directly to the sulphonate group are observable (Table I). These large shifts cannot be explained with the mesomeric or inductive effect of the sulphonate group. On the contrary, relatively small changes in the chemical shifts induced by the sulphonate group relative to naphthalene in ortho-, meta- and para-carbons have been noted. In explaining the changes of these chemical shifts, especially the large shift...
Table I. $^{13}$C chemical shifts of the present disulpho-substituted naphthols relative to the external standard (TMS) at 298 K. The Table also shows the $^{13}$C chemical shifts of naphthalene for comparison.

<table>
<thead>
<tr>
<th>Compound</th>
<th>C-1</th>
<th>C-2</th>
<th>C-3</th>
<th>C-4</th>
<th>Chemical shifts [ppm]</th>
<th>C-5</th>
<th>C-6</th>
<th>C-7</th>
<th>C-8</th>
<th>C-9</th>
<th>C-10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>128.10</td>
<td>125.95</td>
<td>125.95</td>
<td>128.10</td>
<td>128.10  125.95  125.95</td>
<td>128.10</td>
<td>133.70</td>
<td>133.70</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>136 HNDS</td>
<td>153.60</td>
<td>107.45</td>
<td>142.12</td>
<td>119.36</td>
<td>127.50  142.17  124.24</td>
<td>124.24</td>
<td>127.45</td>
<td>133.64</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>138 HNDS</td>
<td>152.76</td>
<td>111.73</td>
<td>141.87</td>
<td>120.04</td>
<td>135.76  126.74  130.08</td>
<td>136.88</td>
<td>121.73</td>
<td>137.38</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>236 HNDS</td>
<td>112.49</td>
<td>153.04</td>
<td>126.75</td>
<td>128.26</td>
<td>127.58  138.95  125.24</td>
<td>130.86</td>
<td>137.95</td>
<td>132.25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>268 HNDS</td>
<td>108.40</td>
<td>157.86</td>
<td>120.75</td>
<td>133.18</td>
<td>130.74  123.70  138.42</td>
<td>131.69</td>
<td>129.23</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

in the carbon attached directly to the sulphonate group, other effects must be taken in account, such as the field or steric effect of this relative bulk functional group. Since there are so many different simultaneous effects, the entire influence of the sulphonate group on the distribution of $\pi$-electrons is a sum of these effects, and hence the contribution of the pure mesomeric effect cannot be resolved.

According to the semi-empirical theory based on the ASMO–CI method\(^5\), the effect of the substitution on the naphthalene MO's depends entirely upon the position where the substituent is attached to the molecule. In 1- and 2-naphthols the electron density is somewhat different in the corresponding carbon nuclei. For example, the $\pi$-electron density around C-2 in 2-naphthol is about 5% greater than that around C-1 in 1-naphthol\(^5\). However, these differences in electron density cannot explain the changes in the differences of the chemical shifts between the corresponding carbon nuclei (being about 23%) in the present compounds (Fig. 1).

In 136 HNDS and 138 HNDS (Fig. 1) the changes in the chemical shifts in the carbons C-1 are about 7 ppm and 2 ppm smaller than those noted in the carbons C-2 in 268 HNDS and 236 HNDS, respectively. This is due to the sulphonate group which is located in ortho-position to the hydroxyl group in 236 HNDS. Because the mesomorphic effect of the sulphonate group is very small, as mentioned above, the other possible effects (e.g. the field and steric effects) diminish the electron density around the carbon C-2.

It has been noted in earlier investigations\(^1,2,4,6-7\) that a negative change is induced through the carbon C-9 to the carbon C-8 by the mesomorphic effect of the hydroxyl group when this group is substituted in carbon C-1 in the naphthalene ring. This is, however, an agent for the abnormal transmission of the mesomeric effect along the carbon chain. Thus, it seems that in 1-naphthols the disturbance of the mesomeric effect changes its "sign" when it is transmitted through the electron cloud of the carbon C-9. The changes in the chemical shifts in the carbons C-8 in 136 HNDS and 138 HNDS are $-3.86$ and $+8.76$ ppm, respectively. In the case of 2-naphthols the change of the chemical shift of the carbon C-8 in 236 HNDS and 268 HNDS is diminished in the former acid ($-2.76$ ppm) and increased in the latter (10.32 ppm) with respect to their absolute values. However, the signs of these shifts are same as in 136 HNDS and 138 HNDS. Thus, it seems that in 2-naphthols the sign rule of the mesomeric effect of the hydroxyl group is quite correct along the carbon nuclei. The explanation for this finding might lie in the fact that the mesomeric effect on the carbon in meta-position is significantly smaller than that on the carbon in para-position\(^6\). On the other hand, the bridge-end in the naphthalene ring seems to disturb the normal progress of the mesomeric effect of the hydroxyl group.
In 136HNDS the sulphonate groups are located in the different halves of the naphthalene ring (in the carbons C-3 and C-6). In comparing the changes of the chemical shifts of 136HNDS induced by the substituents in the carbon C-3 with those of 138HNDS, it can be observed that all the changes in the chemical shifts of 13C nuclei are identical within the limits of accuracy of the measurement. In accordance with the earlier studies, it is observed that in 1-naphthols the change of the chemical shifts is about zero in a carbon in meta-position. In 138HNDS the sulphonate group is attached to the carbon C-3 (in meta-position with regard to the hydroxyl group). Thus, it can be assumed that the change in the chemical shift induced in the carbon C-3 is almost entirely caused by the sulphonate group. Judging from the present measurements, one can further ascertain that the sulphonate groups in position C-3 and C-6 do not disturb each other, because the changes in the chemical shifts induced by these two groups in the carbons C-3 and C-6 are identical, within the limits of accuracy of the measurements, to those in 138HNDS in the carbon C-3. On the other hand, in 268HNDS both the sulphonate groups are located in the same half of the naphthalene ring (in meta-positions to each other), and disturb greatly each other.

In conclusion, one can maintain that in disulpho-substituted 1- and 2-naphthols the hydroxyl group induces great changes in the distribution of the π-electron density around the carbon C-3 are almost equal but reverse, because the two groups are in ortho-position relative to each other.

The sulphonate group induces a great shift towards upfield in the carbon to which it is attached. In the ortho- and meta-carbons the shifts have the same direction towards upfield, but are of relatively small magnitude. The entire influence of these two groups is very complicated, especially when the hydroxyl and sulphonate groups are located in peri-positions relative to each other.

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1 Lauri H. J. Lajunen and Kauko Räisänen, to be published.
2 Kauko Räisänen and Lauri H. J. Lajunen, to be published.
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