Proton Magnetic Resonance Spectra of Some Substituted 2-Acylamino-3-arylamino-1,4-naphthoquinones

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(Z. Naturforsch. 31b, 261-263 [1976]; received September 9, 1975)

N-[3-(p-Chloroanilino)-1,4-dihydro-1,4-dioxo-2-naphthyl]acetamide,
N-[1,4-Dihydro-1,4-dioxo-3-(p-toluidino)-2-naphthyl]acetamide,
N-[1,4-Dihydro-1,4-dioxo-3-(p-phenetidino)-2-naphthyl]acetamide,
N-[1,4-Dihydro-1,4-dioxo-3-morpholino-2-naphthyl]acetamide, PMR

The proton magnetic resonance spectra of a number of substituted 2-acylamino-3-arylamino-1,4-naphthoquinones have been measured and discussed. The effect of various substitution pattern and hetero atoms on the chemical shift values of N-acylmethyl protons have been studied and explained.

Introduction

The wide spread use of naphthoquinones have given rise to extensive investigations of their structures. Since IR and other instrumental techniques will not readily distinguish e.g., isomeric naphthoquinones, substituted naphthoquinones and tautomerism in naphthazarin system, the use of NMR spectroscopy offered an attractive solution to the problem of unambiguous structure assignment of varied naphthoquinones. Although literature is replete\textsuperscript{1-5} with the PMR studies of naphthoquinones. There are no data dealing with PMR spectra of 2-acylamino-3-arylamino-1,4-naphthoquinones.

Experimental

All compounds were of analytical grade and purity was checked by thin layer chromatography using various nonaqueous solvent systems. The NMR spectra were taken at 60 MHz on a varian EM-360 spectrometer in deuterochloroform solution. The concentration of the samples was about 5% by weight. The chemical shift data are expressed in ppm with respect to tetramethylsilane as internal reference assuming equal to zero.

Synthesis of 2-acylamino-3-arylamino-1,4-naphthoquinones (2)

To a hot solution of N-(3-chloro-1,4-dihydro-1,4-dioxo-2-naphthyl)acetamide (1) in 20 ml of 1,4-dioxane was added 0.02 mole of substituted aromatic amine. The solution was refluxed for 2 hours, cooled and poured in 1 l ice cold water. The product was isolated by filtration, recrystallized from benzene (Table I).

Results and Discussion

The aromatic protons in all 1,4-naphthoquinones give a typical A\textsubscript{2}B\textsubscript{2} pattern. The two \(\alpha\)-protons give the signal at lower field from \(\delta = 7.96\) to 8.08 ppm due to combined effect of the anisotropy and strong electron withdrawing character of quinone carbonyls, while the \(\beta\)-hydrogens show a signal at \(\delta = 6.8\) to 7.81 ppm region (Table I). The NH-protons seem to occur\textsuperscript{6,7} at the most downfield side, as the off set and \(\text{D}_2\text{O}\) exchange of the samples was not performed. Hence, it was not possible to locate the position of \(-\text{NH}\) protons in the spectra.

It was found that N-acyl-methyl protons in naphthoquinones (2a-f) appears in \(\delta = 1.56\) to 1.7 ppm region, while the N-acylmethylprotons of 2g and 2h containing morpholino and piperidino substituents respectively appears at \(\delta = 2.23\) ppm.

It appears that the position of N-acyl methyl protons are shifted to higher field by \(\delta = 0.7\) ppm (approximately) than the normal N-acyl methyl protons\textsuperscript{6,7} (Table I). It may be due to the coplanarity of the anilino nucleus with naphthoquinone nucleus and due to mesomorphic effect (resonance effect) of anilino nucleus donating electron density toward the naphthoquinone nucleus, which in turn by long range coupling shielded the N-acyl methyl group, so
invariably in compounds 2a-f we observed COCH$_3$ resonance at $\delta = 1.56$ to 1.70 ppm. In contrast to this in compounds 2g and 2h which contain the morpholino and piperidino group respectively have no contribution toward resonance or shielding so the position of COCH$_3$ protons occurs at the normal$^{6,7}$ position.

The aromatic protons of 3-substituted ring in

<table>
<thead>
<tr>
<th>Compound</th>
<th>m.p. [°C]</th>
<th>COCH$_3$ [ppm]</th>
<th>Aromatic protons of naphthoquinone $\alpha$ [ppm]</th>
<th>$\beta$ [ppm]</th>
<th>Position of the substituent in 3-substituted ring [ppm]</th>
<th>Aromatic protons of the 3-substituted ring $\alpha + \alpha'$ [ppm]</th>
<th>$\beta + \beta'$ [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>203–204</td>
<td>1.56 (S)</td>
<td>8.03 (mc)</td>
<td>7.76 (mc)</td>
<td>--</td>
<td>6.87–7.33 (not resolved)</td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td>195</td>
<td>1.66 (S)</td>
<td>8.06 (mc)</td>
<td>7.78 (mc)</td>
<td>9 $a + a'$ 6.80 (d)</td>
<td>6 $b + b'$ 7.22 (d)</td>
<td></td>
</tr>
<tr>
<td>2c</td>
<td>185</td>
<td>1.70 (S)</td>
<td>8.06 (mc)</td>
<td>7.81 (mc)</td>
<td>9 $a + a'$ 6.77 (d)</td>
<td>9 $b + b'$ 7.37 (d)</td>
<td></td>
</tr>
<tr>
<td>2d</td>
<td>145</td>
<td>1.66 (S)</td>
<td>8.08 (mc)</td>
<td>7.76 (mc)</td>
<td>--</td>
<td>6.8–7.03 (not resolved)</td>
<td></td>
</tr>
<tr>
<td>2e</td>
<td>190</td>
<td>1.56 (S)</td>
<td>8.06 (mc)</td>
<td>7.73 (mc)</td>
<td>2.3 (S)–(CH$_3$)</td>
<td>6.8–7.32 (not resolved)</td>
<td></td>
</tr>
<tr>
<td>2f</td>
<td>148–150</td>
<td>1.56 (S)</td>
<td>8.03 (mc)</td>
<td>7.73 (mc)</td>
<td>1.38 (t)–(CH$_3$) $J = 7$ 4.0 (q)–(CH$_3$) $J = 6$</td>
<td>6.7–7.2 (not resolved)</td>
<td></td>
</tr>
<tr>
<td>2g</td>
<td>203</td>
<td>2.23 (S)</td>
<td>7.96 (mc)</td>
<td>7.63 (mc)</td>
<td>--</td>
<td>$a + a' 3.41$ (t) $J = 5$</td>
<td>$b + b' 3.81$ (t) $J = 5$</td>
</tr>
<tr>
<td>2h</td>
<td>178</td>
<td>2.23 (S)</td>
<td>7.96 (mc)</td>
<td>6.8 (mc)</td>
<td>--</td>
<td>$a + a' 3.40$ (S) $b, b' + b'' 1.66$ (mc)</td>
<td></td>
</tr>
</tbody>
</table>

S = Singlet; d = doublet; t = triplet; q = quartet; mc = multiplet centre.
$J_0$ = ortho coupling; $J$ = coupling constant.
compound 2a appeared between $\delta = 6.87$ to 7.33 ppm region and confirmed on the integration curve of 2a and could not be resolved individually. Firstly because of the low resolution of the instrument used and secondly due to the low solubility of the sample in deutrated solvent used.

In the NMR spectra of N-[3-(p-chloroanilino)-1,4-dihydro-1,4-dioxo-2-naphthyl]acetamide (2b) symmetrical aromatic protons $H_a$, $H_a'$ and $H_b$, $H_b'$ appeared as doublets. The aromatic protons $H_b$ and $H_b'$ adjacent to chloro group appeared as sharp doublet centered at ($J_0 = 9$) $\delta = 7.22$ ppm. This is due to the high electronegativity of the chlorine the resonance of the $H_b$ and $H_b'$ protons deshielded, while the aromatic protons $H_a$ and $H_a'$ adjacent to NH group again appeared as a doublet centered at ($J_0 = 9$) $\delta = 6.80$ ppm.

The aromatic protons $H_b$ and $H_b'$ of N-[3-(p-bromoanilino)-1,4-dihydro-1,4-dioxo-2-naphthyl]acetamide (2c) appeared as a doublet centered at ($J_0 = 9$) $\delta = 7.37$ ppm, while the aromatic protons adjacent to NH group appeared as a doublet centered at ($J_0 = 9$) $\delta = 6.77$ ppm. The aromatic protons of 3-substituted ring in compound 2d appeared between $\delta = 6.8$ to 7.03 ppm region (Table I) and could not be resolved individually.

PMR spectra of N-[1,4-dihydro-1,4-dioxo-3-(p-toluidino)-2-naphthyl]acetamide (2e), showed the methyl protons as a sharp singlet at $\delta = 2.3$ ppm. The higher field doublet centered at $\delta = 6.81$ ppm ($J_0 = 8$) is due to aromatic protons $H_a$ and $H_a'$ adjacent to NH group, while the protons $H_b$ and $H_b'$ adjacent to methyl group appeared as a doublet centered at $\delta = 7.08$ ppm ($J_0 = 8$). The spectrum is quite comparable to those discussed earlier, except to the position of the $-\text{CH}_3$ group in place of halogen group. The resonance of $H_b$ and $H_b'$ protons is slightly shielded in contrast to corresponding protons of 2b-d due to the electron donating nature of methyl group (Table I).

PMR spectra of N-[1,4-dihydro-1,4-dioxo-3-(p-phenetidino)-2-naphthyl]acetamide (2f) showed that the methyl part of ethoxy group appeared as a triplet centered at $\delta = 1.38$ ppm, the coupling constant ($J$ in cps) was to be 7, while the methylene part appeared as quartet at $\delta = 4.0$ ppm ($J = 6$). The aromatic protons appeared in the range $\delta = 6.7$ to 7.2 ppm, and could not be resolved.

PMR spectra of N-(1,4-dihydro-1,4-dioxo-3-morpholino-2-naphthyl]acetamide (2g) (Fig. 1) gave the downfield methylene protons adjacent to oxygen as a triplet centered at $\delta = 3.81$ ppm ($J = 5$). This could be explained due to the fact they are adjacent to an element having higher electronegativity in comparison to nitrogen. The methylene protons adjacent to nitrogen appeared as a triplet ($J = 5$) centered at $\delta = 3.41$ ppm.

The methylene protons of the piperidino ring (2h) appeared in two regions. The two methylene protons adjacent to nitrogen appeared as a singlet at $\delta = 3.4$ ppm, while the rest of three methylene group protons appeared at $\delta = 1.66$ ppm.

We thank the CSIR, New Delhi for the financial assistance.