Chirality in $\alpha$-Dinitrophenyl $\beta$-Keto Esters

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Chirality in α- Dinitrophenyl –β– Keto Esters

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ABSTRACT

The complex methylene pmr spectra of some α- dinitrophenyl-β- keto esters is explained in terms of chirality of the molecules due to hindered rotation about aromatic carbon-aliphatic carbon bond. pmr and cmr data is reported in order to prove the conclusions.

INTRODUCTION

The NMR spectra of compounds which contain the groups – CH₂ X– or –C(CH₃)₂ X have been investigated by numerous authors and an excellent review of the subject has been given by Raban and Mislow¹. Molecules which are chiral but not asymmetric may contain diastereotopic groupings. Nuclei which are diastereotropic must have different chemical shifts in either chiral or chiral solvents. Such nuclei are said to be anisochronous such as diethyl sulfite², cyclocarbinyl ethyl ether³ offer striking examples of magnetic nonequivalence of methylene hydrogens in compounds of the type R-CH₂ –O–CR₁ R₂ R₃. Thus the pmr spectra of such methylene protons are often typical of AB rather then A₂ systems.¹

In our studies, the investigation of enolisation of α-dinitrophenyl-β-keto esters by pmr we observed that the some of enolic form of said molecules exhibit complex methylene spectra and that was explained in terms of chirality due to the hindered rotation about aromatic carbon-enolic carbon bond.

¹ Mailing Address; Diyarbakır Fen Fakültesi, Kimya Bölümü, Diyarbakır, Turkey
Figure-I. 60 MHz pmr spectra of α-2, 4-dinitrophenyl ethylacetoacetate in CDCl₃ (5 % Wt/vol) 40°C Offset 360 Hz.
Figure-II. 60 MHz pnm spectra of α-2, 4-dinitrophenyl ethylacetacetae in CF$_3$COOH (5 % Wt/vol) at 40°C.
RESULTS AND DISCUSSIONS

Regarding both cmr and pmr spectra it seems strongly justified that α-dinitrophenyl-β-keto esters are at least 90% enolic (Figure 1). However in strongly acidic solvents keto content of such molecules increase up to 40% (Figure II).

It is now also proved that enol from of α-2, 4-dinitrophenyl-β-keto esters exhibit biphenyl-like-isomerism due to the chelation of β-keto esters obviously behave as a plane which would be prevented to rotate about aromatic carbon-enolic carbon bond.

![Image of molecular structure]

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>R</th>
<th>R'</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>CH₃</td>
<td>CH₃</td>
</tr>
<tr>
<td>II</td>
<td>CH₃</td>
<td>C₆H₄NO₂</td>
</tr>
</tbody>
</table>

Chirality of the molecule arises from the chelate ring of the β-keto esters because of the observation that in the presence of piperidin the complex ABC₃ spectra of compound-I simplified to A₂B₃ spectra due to intra molecular proton transfer which decrease the stability of chelate ring resulting the rotation about the Cα-COOR bond.

Hence, two rings in compound-I and II could not be coplanar due to impingement of the o-nitro group of phenyl ring as well as 1, 3-substituents of chelate ring.
An O-substituent of one ring thus is located above the plane of the second ring, and if the second ring holds two different o-groups or 1, 3-substituents the substituents on the first ring is in an asymmetric environment. If that substituents contains methylene group its two protons thus become diastereotopic. Therefore methylene protons on ethoxy groups of α-2, 4-dinitrophenyl-β-keto ethyl esters are diastereotopic and hence anisochronous. In such a case ABC₃ (or ABX₃) spin systems are expected and observed. Diastereotopic methylene protons resides in different environment even though the substituent rotates about chelate ring-substituent bond. The conformers of the ethoxy group about that bond (e.g., Ia-d Fig. III) will not necessarily be equally populated and the environments of the two protons are different in each conformer.

Figure – III. Conformers of chiral α- dinitrophenyl- β- keto esters

This could be seen from the pmr spectra of α-2, 4-dinitrophenyl acetoacetate (compound-I) in which the pmr spectra of such methylene protons typical AB rather than A₂ systems and complex spectra characteristic of AB part of ABC₃ spectra. The chemical shift between the two anisochronous protons Δδₐᵦ varies from 2 Hz to 11 Hz depending on the solvent and the structure of compound at 60 MHz with methyl-methylene coupling constants ca. 7, 0 Hz (Table-II).

After series of iterative calculations it was also demonstrated that methylene spectrum of compound-I could be fitted to with in experimental error although there is a lower limit to Δδₐᵦ below which instrument resolution do not permit us. Therefore it was
Table I. Chemical Shifts and Coupling Constants of Ethoxyl Protons of chiral α- dinitrophenyl – β- keto esters, Compound-I and II in CDCl₃, 40°C, Values Hz down field from internal TMS at 60 MHz.

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>R'</th>
<th>δHₐ</th>
<th>δHₖ</th>
<th>δH_AB</th>
<th>J_AB</th>
<th>δ_C</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>CH₃</td>
<td>CH₃</td>
<td>246.2</td>
<td>255.6</td>
<td>9.4</td>
<td>10.5</td>
<td>70</td>
</tr>
<tr>
<td>II</td>
<td>N₀, C₄ H₄</td>
<td>CH₃</td>
<td>250.0</td>
<td>261.0</td>
<td>11.0</td>
<td>10.0</td>
<td>72</td>
</tr>
</tbody>
</table>

estimated ca. 2 Hz was the minimum value for the separations in theoretically calculated spectra (Figure-IV). Signs of coupling constants are, of course, assigned by analogy⁸ (Figure-IV).

The origin of this magnetic nonequivalence has been subject of several investigations and two distinct chemical shift effects have been reported¹,² a). An intrinsic asymmetry effect ……. independent of rotamer populations b). Shift differences caused by dissimilar populations of various conformations or rotamers. It is still in question whether the former or the latter is alone responsible for magnetic nonequivalence. However, in our case effect of hindered rotations in the molecule is quite apparent.

Therefore we also examined pmr spectra of the similar compounds. The simple A₂B₃ methylene spectra of α– 2, 6-dinitrophenyl-β-keto esters (compound – III, IV) strongly proves that anisoisochronous behavior of methylene protons determined by the dissimilar o-substituents just as in biphenyl isomerism, similarly, 3– (2, 4-dinitrophenyl)-2, 4-pentandion (V) and α– 2, 4-dinitrophenylethylcyanooacetate (VI) give simple A₂B₃ spectra of ethyl group although the fact that the molecule is asymmetrical and likely to be the racemic mixture. It is also interesting to note that α– (2, 4-dinitrophenyl)-t-butyl acetoacetate (VII) gives a line from t-butyl group due to the enantiotopic methyl groups-indicating that contribution of rotamers about the oxygen-carbon bond is quite significant on magnetic nonequivalence (Table-II), (Figure-III) which is although not affected from the rotations about oxygen-carbonyl bond that seems also restricted.

The most important factor for the magnitudes of the shift differences anisotropy associated with phenyl ring, nitro groups as well as unsaturated chelate ring. The $^{13}$C magnetic resonance spectra of compound-I and II was also examined (Table-III).
Figure IV. Observed and calculated pmr spectra of 10 % wt/vol solution of α- 2, 4-dinitrophenyl ethyl acetoacetate in CDCl₃ at 60 MHz TMS as an internal reference taken as zero.
Table II. pmr data of some α-dinitrophenyl-β-keto esters in CDCl₃ at 40°C. (II)

![Chemical Structure](image)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>δR₁</th>
<th>δR₂</th>
<th>δCH₃</th>
<th>δRₓ</th>
<th>δHₐ</th>
<th>δHₐ</th>
<th>δX</th>
<th>δY</th>
<th>δOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>(III) α-2, 6-dinitrophenyl ethyl acetocacetate</td>
<td>250</td>
<td>250</td>
<td>67</td>
<td>107</td>
<td>482</td>
<td>482</td>
<td>458</td>
<td>—</td>
<td>777</td>
</tr>
<tr>
<td>(IV) α-2, 6-dinitrophenyl ethyl benzoylacetate</td>
<td>253</td>
<td>253</td>
<td>71</td>
<td>428</td>
<td>468</td>
<td>468</td>
<td>452</td>
<td>—</td>
<td>798</td>
</tr>
<tr>
<td>(V) 3-(2, 4-dinitrophenyl)-2, 4-pentandion</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>110</td>
<td>508</td>
<td>524</td>
<td>—</td>
<td>469</td>
<td>980</td>
</tr>
<tr>
<td>(VI) α-2, 4-dinitrophenylethylcyclooctetacetate</td>
<td>256</td>
<td>256</td>
<td>76</td>
<td>—</td>
<td>518</td>
<td>534</td>
<td>—</td>
<td>484</td>
<td>334(x)</td>
</tr>
<tr>
<td>(VII) α-2, 4-dinitrophenyl butyric acid</td>
<td>83</td>
<td>83</td>
<td>83</td>
<td>117</td>
<td>504</td>
<td>523</td>
<td>—</td>
<td>452</td>
<td>809</td>
</tr>
</tbody>
</table>

(II) Chemical shift values are in Hs, aromatic protons given were calculated according to the first order approach for ABX pattern, and denoted by the delta scale, low fields shifts are shown as positive values relative to TMS as internal reference. Concentration of substance taken 2% – 5% in volume.

(X) Chemical shift value of methine proton.

PMR spectra were run on a VARIAN Associate Model A-60A spectrometer operating a frequency of 60 MHz.
Table III. $^{13}$C Chemical shifts and relative intensities of compound-I and compound-II expressed in ppm from TMS internal reference(x)

![Diagram](image)

<table>
<thead>
<tr>
<th>No$^{13}$C</th>
<th>Compound-I $\delta^{13}$C</th>
<th>Int.</th>
<th>Compound-II $\delta^{13}$C</th>
<th>Int.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>174.2</td>
<td>56</td>
<td>169.8</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>169.9</td>
<td>54</td>
<td>- 169.4</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>150.0</td>
<td>16</td>
<td>149.6</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>148.0</td>
<td>20</td>
<td>136.9</td>
<td>12</td>
</tr>
<tr>
<td>a</td>
<td>-</td>
<td>-</td>
<td>148.7</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>136.5</td>
<td>33</td>
<td>139.4</td>
<td>38</td>
</tr>
<tr>
<td>b</td>
<td>-</td>
<td>-</td>
<td>135.8</td>
<td>107+</td>
</tr>
<tr>
<td>c</td>
<td>-</td>
<td>-</td>
<td>129.0</td>
<td>203</td>
</tr>
<tr>
<td>6</td>
<td>135.6</td>
<td>171</td>
<td>135.8</td>
<td>107+</td>
</tr>
<tr>
<td>7</td>
<td>126.8</td>
<td>179</td>
<td>126.7</td>
<td>81</td>
</tr>
<tr>
<td>d</td>
<td>-</td>
<td>-</td>
<td>123.0</td>
<td>154</td>
</tr>
<tr>
<td>8</td>
<td>120.0</td>
<td>171</td>
<td>120.0</td>
<td>75</td>
</tr>
<tr>
<td>9</td>
<td>99.8</td>
<td>59</td>
<td>102.0</td>
<td>17</td>
</tr>
<tr>
<td>10</td>
<td>61.4</td>
<td>180</td>
<td>62.5</td>
<td>103</td>
</tr>
<tr>
<td>11*</td>
<td>20.0</td>
<td>152</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>13.6</td>
<td>205</td>
<td>13.6</td>
<td>100</td>
</tr>
</tbody>
</table>

(x) Spectra were run on a VARIAN model XL-100 spectrometer operating in FT mode 25, 18 MHz.

(b) Aromatic carbon adjacent to carbonyl carbon in compound

(±) Total relative intensity of Carbon-b and Carbon-6 since the signals are superimposed

(*) Carbon of methyl group in Compound-I

There is no signal separation at aliphatic range of the spectrum although the fact that shift differences between conformers are large and $^{13}$C chemical shifts are extremely sensitive to constitutional environment.
ACKNOWLEDGEMENT

The work partly carried out at N.T.H. Norway while the author granted by NORAD is greatly Acknowledged. $^{13}$C spectra were run by Dr. F.W. Wehrli from VARIAN AG, Zug.

REFERENCES

1. K. Mislow and M. Rahan, Top. Stereochem. 1,1 (1967)

ÖZET

α- dinitrofenil – β- keto esterlerin metilen grubunun karmarış pmr spektrumunun kaynağı tartışılması ve alifatik-aromatik karbon atomları arasındaki bağı etrafındaki dönmenin yapışal engellenmeler nedeni ile sınırlandığı ve "bifenil" izomerlerine benzer "chiral" bir yapı oluşturduğu bu nedenle metilen protonlarının "diasterotopik" olarak davranlıklar anlaşılmuştur. Ayrıca bazı molekülerde teorik yaklaşımlar ile pmr sabitleri bulunmuş denel sonuçlar ile karşılaştırmalıdır.
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