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CONFORMATIONAL PREFERENCE
OF CIS-1-ARYL-2-(2-BENZO[C]PHENANTHRYL)-
AND CIS-1-ARYL-2-(3-PHENANTHRYL)-ETHENES

BY

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NMR measurements under different conditions (temperature, solvents used, presence of a shift-reagent) of cis- and trans-1-aryl-2-(2-benzo[c]phenanthryl)-ethenes reveal that an overcrowded conformation predominates in cis isomers. In the analogous 1-aryl-2-(3-phenanthryl)ethenes no clear conformational preference is found.

In connection with investigations on the formation and properties of helicenes1,2,3 we were interested in the conformational equilibria of diarylethenes, used in the syntheses of helicenic molecules. To this aim we investigated the NMR spectra of several cis-trans pairs of arylbenzo[c]phenanthrylethenes (I-VI) and arylphenanthrylethenes (VII-X).

Güsten and Salzwedel found4 that δ-values of olefinic and aromatic protons in substituted cis-stilbenes are always larger than in corresponding trans compounds as a consequence of mesomeric effects in the non-planar cis isomers. However, in diarylolefines having larger aryl residues the steric relationships between cis and trans isomers are much more complicated.

For cis-I two extreme conformations are possible, cis-IA or cis-syn- and cis-IB or cis-anti-, which interchange by rotation around the Cₐ-C₃ axis. (In cis-II, -III, -IV, -VIII and -IX four conformations are possible because also rotation around the C₃-C₄ axis leads to different conformations.) Although neither IA nor IB can be completely planar,

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crowding in IA will be much more serious. Therefore, IB seems to be preferred to IA. The most important conformations of the trans isomer (IC and ID) are both coplanar.

I Ar=phenyl*
II β-naphthyl
III α-naphthyl
IV 1-(8-methyl)naphthyl
V 4-methoxyphenyl
VI 4-hydroxymethylphenyl
VII Ar=phenyl
VIII β-naphthyl
IX 3-phenanthryl
X 4-hydroxymethylphenyl

* The numbering of the benzo[c]phenanthrene moiety, which is not in accordance with IUPAC-rules, has been chosen in order to simplify tabulation of data from both series I-VI and VII-X (see Tables I-IV).
It can be assumed that protons 5, 6 and 7 in the cis-syn forms (A) are shifted upfield if compared with the corresponding protons in conformations C and D of the trans isomers. This will not be the case in the cis-anti forms (B).

A comparison of the NMR spectra of the cis-trans isomers investigated shows that in trans isomers of compounds I-VI the angular protons 4 and 5 have about the same chemical shift value (8.9–9.1, Table I); in the cis-isomers they are clearly separated (Δδ: 0.44–0.80 ppm). A similar difference was found for angular protons 4 and 5 in the phenanthrene series VII-X: coinciding α₃-protons in trans compounds, δ = 8.6–8.8, but in cis isomers Δδ = 0.20–0.25 ppm. In both series the multiplets of the other aromatic protons are much more extended to higher field in the spectra of cis than in those of trans isomers.

By spin decoupling δ-values of several protons could be determined accurately. These values are given in Table I, together with differences in δ-values (Δδ) of the corresponding protons in cis-trans isomers. The Δδ-values of ethenic protons (about 0.50 ppm) are equal to those found in stilbene derivatives. The spin-spin coupling constants of α- and β-protons are $J_{cis}12.0 \pm 0.5$ and $J_{trans}16.0 \pm 0.5$.

Δδ-values of 2'- and 3'-protons in V and VI (0.16 and 0.12, respectively) are rather small in comparison with those found in para-substituted stilbenes (0.25 and 0.16, respectively). This may be due to a reduction of the mesomeric influence of the substituent on the ring positions 2' and 3'. This might be a consequence of the large polarisability of the benzphenanthryl residue in our series.

The large Δδ-values found for protons 5 and 6 in compounds I-VI suggest that the cis isomers are predominantly in the sterically unfavoured cis-syn conformation. The largest Δδ-values are found in the...
Table I

Chemical shifts (δ in ppm) of protons in cis and trans isomers of compounds 1-X, and differences in chemical shifts (Δδ) between corresponding protons in cis-trans isomers, measured in CS₂ solution.

<table>
<thead>
<tr>
<th>Benzo[c]phenanthrene series</th>
<th>Proton:</th>
<th>α,β</th>
<th>2'</th>
<th>3'</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>CH₃ or CH₂X</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>cis</td>
<td>6.72</td>
<td>8.83</td>
<td>8.33</td>
<td>7.18</td>
<td></td>
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<td></td>
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<tr>
<td></td>
<td>trans</td>
<td>7.23</td>
<td>8.96</td>
<td>9.00</td>
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<td></td>
<td>Δδ</td>
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<td>0.67</td>
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<td>II</td>
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<td>8.78</td>
<td>8.06</td>
<td>6.44</td>
<td>7.20</td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>trans</td>
<td>7.34</td>
<td>9.03</td>
<td>9.06</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Δδ</td>
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<td>0.25</td>
<td>1.00</td>
<td>1.14</td>
<td></td>
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<td></td>
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<tr>
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<td>7.05</td>
<td>8.70</td>
<td>7.98</td>
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<td>9.03</td>
<td>7.61</td>
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<tr>
<td>IV</td>
<td>cis</td>
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<td>7.80</td>
<td>7.98</td>
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<tr>
<td></td>
<td>Δδ</td>
<td>0.36</td>
<td>1.05</td>
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<td></td>
<td>0</td>
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<td>V</td>
<td>cis</td>
<td>6.62</td>
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<td>6.67</td>
<td>8.79</td>
<td>8.35</td>
<td>3.62</td>
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<td>7.38</td>
<td>6.78</td>
<td>8.92</td>
<td>8.99</td>
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<td>Δδ</td>
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<td>0.11</td>
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<td>0.64</td>
<td>0.13</td>
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<td>VI</td>
<td>cis</td>
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<td>7.25</td>
<td>7.14</td>
<td>8.79</td>
<td>8.26</td>
<td>4.49</td>
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<tr>
<td></td>
<td>trans</td>
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<td>7.42</td>
<td>7.27</td>
<td>8.97</td>
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<td>4.57</td>
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<tr>
<td></td>
<td>Δδ</td>
<td>0.48</td>
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<td>0.18</td>
<td>0.76</td>
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<th>3'</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>CH(_3) or CH(_2)X</th>
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<tr>
<td>VII</td>
<td>cis</td>
<td>6.81</td>
<td>7.36</td>
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<td>0.16</td>
<td>0.38</td>
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<td>trans</td>
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<td>7.36</td>
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<td>0.16</td>
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<td>8.74</td>
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</tr>
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<td></td>
<td>(\Delta\delta)</td>
<td>6.94</td>
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<td>8.62</td>
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</tr>
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<td>cis</td>
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<td>8.62</td>
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<td></td>
</tr>
<tr>
<td>VIII</td>
<td>cis</td>
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<td>7.51</td>
<td>0.57</td>
<td>8.66</td>
<td>8.80</td>
<td>8.78</td>
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<td>8.78</td>
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<td>cis</td>
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<td>0.57</td>
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<td>8.80</td>
<td>8.78</td>
<td>0.14</td>
<td>0.38</td>
</tr>
<tr>
<td>IX</td>
<td>(\Delta\delta)</td>
<td>7.02</td>
<td></td>
<td></td>
<td>8.80</td>
<td>8.80</td>
<td>8.78</td>
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<tr>
<td>X</td>
<td>cis</td>
<td>6.69, 6.86</td>
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<td>8.55</td>
<td>8.21</td>
<td>0.34</td>
<td>0.38</td>
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<tr>
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<td>8.55</td>
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<td>8.55</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\Delta\delta)</td>
<td></td>
<td></td>
<td>0.14</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All NMR spectra were recorded with a Varian HA 100 spectrometer.
naphthyl derivatives II-IV, in which the additional ring apparently causes stronger shielding of these protons in the cis-isomers.

The striking resemblance between the preferred conformation of the cis isomers and hexahelicene is illustrated in Fig. 1.

Fig. 1. \( \delta \) values of corresponding protons in cis isomers I-III and hexahelicene.

In the phenanthrene series (VII-X) preference for the cis-syn conformation in cis isomers seems to be much less pronounced. The \( \Delta \delta \)-values of proton 5, which are lower than in compounds I-VI, appear to be independent of the size of the aryl residue. A comparison with a helical molecule as given in Fig. 1 is not possible in this series.

Another indication that at least in the cis isomers of the benzo-phenanthrene series a helical conformation is the preferred one, was found in the temperature dependence of their NMR spectra. As demonstrated in Fig. 2 for cis- and trans-III, on decrease in temperature all peaks shift to higher field but to a strongly varying degree. In Table II the temperature-dependence of \( \delta \)-values for several protons in compounds I-IV, VII and VIII are given.
Table II

Temperature dependence of chemical shifts (ppm 10^5/°C) in CS$_2$ solutions between 25° and −70°C. (Negative values mean upfield shifts on lowering of temperature.)

<table>
<thead>
<tr>
<th></th>
<th>$\alpha,\beta$</th>
<th>$\gamma$</th>
<th>$\delta$</th>
<th>$\epsilon$</th>
<th>$\zeta$</th>
<th>$\eta$</th>
<th>$\iota$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cis trans</td>
<td>cis trans</td>
<td>cis trans</td>
<td>cis trans</td>
<td>cis trans</td>
<td>cis trans</td>
<td>cis trans</td>
</tr>
<tr>
<td>I</td>
<td>−0.04 0</td>
<td>−0.11</td>
<td>−0.11</td>
<td>−0.23</td>
<td>−0.04</td>
<td>−0.10</td>
<td>−0.06</td>
</tr>
<tr>
<td>II</td>
<td>0.0 −0.02</td>
<td>−0.10</td>
<td>−0.11</td>
<td>−0.27</td>
<td>−0.06</td>
<td>−0.39</td>
<td>−0.06</td>
</tr>
<tr>
<td>III</td>
<td>−0.02 +0.11</td>
<td>−0.10</td>
<td>−0.18</td>
<td>−0.22</td>
<td>−0.06</td>
<td>−0.16</td>
<td>−0.27</td>
</tr>
<tr>
<td>IV</td>
<td>−0.03 +0.01</td>
<td>+0.11</td>
<td>−0.33</td>
<td>+0.08</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VII*</td>
<td>−0.03 +0.07</td>
<td>+0.05</td>
<td>+0.05</td>
<td>+0.13</td>
<td>+0.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VIII*</td>
<td>+0.03</td>
<td>+0.07</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

* Measured in AsCl$_3$.

Table III

Temperature-effect on chemical shift of protons in compound II, measured in different solvents (ppm 10^5/°C).

<table>
<thead>
<tr>
<th></th>
<th>$\alpha,\beta$</th>
<th>$\gamma$</th>
<th>$\delta$</th>
<th>$\epsilon$</th>
<th>$\zeta$</th>
<th>$\eta$</th>
<th>$\iota$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cis trans</td>
<td>cis trans</td>
<td>cis trans</td>
<td>cis trans</td>
<td>cis trans</td>
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<tr>
<td>CS$_2$</td>
<td>0 −0.02</td>
<td>−0.10</td>
<td>−0.11</td>
<td>−0.27</td>
<td>−0.06</td>
<td>−0.39</td>
<td>−0.06</td>
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<tr>
<td>diglyme</td>
<td>+0.08 +0.02</td>
<td>−0.06</td>
<td>0</td>
<td>−0.26</td>
<td>0</td>
<td>−0.33</td>
<td>−0.02</td>
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<tr>
<td>DMSO</td>
<td>−0.05 −</td>
<td>−0.11</td>
<td>−0.07</td>
<td>−0.27</td>
<td>0.06</td>
<td>−0.36</td>
<td>−0.08</td>
</tr>
</tbody>
</table>
Fig. 2. Temperature effect on the chemical shifts of protons $\alpha$, $\beta$, 4, 5 and 6 in cis and trans III (\(\Delta\delta\) in ppm).

It is improbable that the large effect on the chemical shift of protons 5 and 6 in compounds I-IV arises from specific solvent effects. The temperature dependence of all protons in hexahelicene, measured in the same solvent was found to be lower than 0.01 (ppm 10\(^2/\degree\)C); for protons 4 and 5 of 3-methylbenzo[c]phenanthrene (numbering as in our formulae) values of 0.06 and 0.04, respectively, were found. Moreover, a quite similar temperature dependence was found for protons 5 and 6 in varying solvents, as shown in Table III for compound II.

Therefore, the upfield shifts of protons 5 and 6 in cis compounds I-IV on decrease in temperature seem to be due to a shift in the conformational equilibrium in the direction of the cis-syn form.

For a final check we measured NMR spectra of the cis and trans isomers of VI and X in the presence of a shift reagent, tris(dipivalomethanato)praseodymium.

An exact analysis of these data is not possible because the influence of the reagent on peaks of various protons depends not only on their distance to the praseodymium atom but also on the relevant H—Pr—O angle which is not known. Moreover, a possible influence of the reagent on the conformational equilibria has been neglected.
Fig. 3. Influence of the shift reagent Pr(DPM)$_3$ on δ-values of protons in cis and trans VI (δ in ppm; solvent CS$_2$).

In Fig. 3 shifts of several protons in cis and trans VI are given in dependence on the mol, ratio Pr(DPM)$_3$/VI. In Table IV the shifts of protons in compounds VI and X are given relative to that of proton 3'. These data suggest that in cis VI proton 6 is much closer to Pr than 2-H or 4-H. The data on cis X are not conclusive; the position of the 6-H signal could not be determined exactly due to overlap by other protons.

Table IV

Shifts of proton peaks caused by the shift reagent tris(dipivalomethanato)praseodymium, relative to the shift of 3'-H measured in CS$_2$.

<table>
<thead>
<tr>
<th>protons:</th>
<th>2'</th>
<th>3'</th>
<th>α</th>
<th>β</th>
<th>2</th>
<th>4</th>
<th>5</th>
<th>6</th>
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<tbody>
<tr>
<td>cis VI</td>
<td>0.33</td>
<td>1</td>
<td>0.12</td>
<td>0.19</td>
<td>0.15</td>
<td>0.15</td>
<td>0.19</td>
<td>0.28</td>
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<tr>
<td>trans VI</td>
<td>0.30</td>
<td>1</td>
<td>0.17</td>
<td>0.16</td>
<td>0.06</td>
<td>0.08</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>cis X</td>
<td>0.33</td>
<td>1</td>
<td>0.12</td>
<td>0.19</td>
<td>0.18</td>
<td>0.14</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>trans X</td>
<td>0.33</td>
<td>1</td>
<td>0.18</td>
<td>0.18</td>
<td></td>
<td>0.08</td>
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</tr>
</tbody>
</table>

From these results it can be concluded that the cis isomers of compounds I-VI exist mainly in the overcrowded conformations*. Com-

parison of δ-values of corresponding protons in hexahelicene and in cis-I shows that at room temperature about 80% of the latter compound will be in the syn conformation A. We assume that the preference for an overcrowded conformation is caused by van der Waals interactions between the aryl residues. It is remarkable that a similar conformational preference is not found in the cis compounds VII-X. This difference might be due to a lower polarizability of the phenanthrene moiety in comparison with the benzo[c]phenanthrene group.

Acknowledgement

We are indebted to Mrs. L. van Herpen-de Cock for measuring the NMR spectra.

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