

PDF hosted at the Radboud Repository of the Radboud University Nijmegen

The following full text is a publisher's version.

For additional information about this publication click this link.

<http://hdl.handle.net/2066/143015>

Please be advised that this information was generated on 2018-07-07 and may be subject to change.

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

BY

M. H. DE JONG and W. H. LAARHOVEN*

(Department of Organic Chemistry, Catholic University, Toernooiveld, Nijmegen,
The Netherlands)

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 helicenes^{1,2,3} 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 C₂-C₃ axis. (In *cis*-II, -III, -IV, -VIII and -IX four conformations are possible because also rotation around the C_β-C_{Ar} axis leads to different conformations.) Although neither IA nor IB can be completely planar,

* To whom inquiries should be addressed.

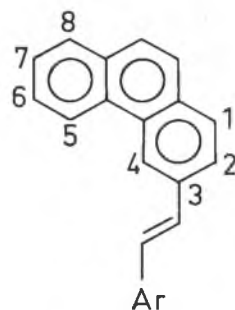
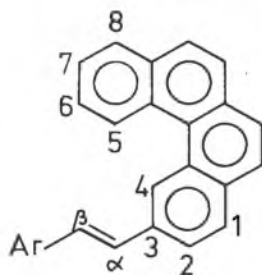
¹ W. H. Laarhoven, Th. J. H. M. Cuppen and R. J. F. Nivard, *Tetrahedron* **26**, 4865 (1970).

² W. H. Laarhoven and R. J. F. Nivard, *ibid.* **28**, 1803 (1972).

³ W. H. Laarhoven and Th. J. H. M. Cuppen, *Recl. Trav. Chim. Pays-Bas*, **92**, 553 (1973)
W. H. Laarhoven and M. H. de Jong, *Recl. Trav. Chim. Pays-Bas* **92**, 651 (1973)

⁴ H. Güsten and M. Salzwedel, *Tetrahedron* **23**, 173, 187 (1967).

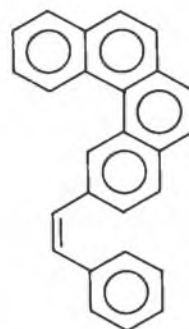
crowding in IA will be much more serious. Therefore, IB seems to be preferred to IA. The most important conformations of the *trans* isomer (IC and ID) are both coplanar.



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

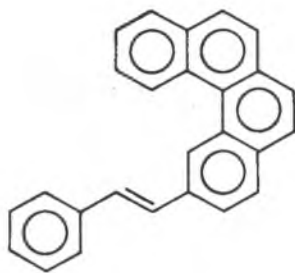


IA *cis* "syn"



IB *cis* "anti"

* 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).

IC *trans* "syn"ID *trans* "anti"

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 ($\Delta\delta$: 0.44–0.80 ppm). A similar difference was found for angular protons 4 and 5 in the phenanthrene series VII-X: coinciding α_3 -protons in *trans* compounds, $\delta = 8.6$ –8.8, but in *cis* isomers $\Delta\delta = 0.20$ –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 ($\Delta\delta$) of the corresponding protons in *cis-trans* isomers. The $\Delta\delta$ -values of ethenic protons (about 0.50 ppm) are equal to those found in stilbene derivatives⁴. The spin-spin coupling constants of α - and β -protons are $J_{cis} 12.0 \pm 0.5$ and $J_{trans} 16.0 \pm 0.5$.

$\Delta\delta$ -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 stilbenes⁴ (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 $\Delta\delta$ -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 $\Delta\delta$ -values are found in the

Table I

Chemical shifts (δ in ppm) of protons in *cis* and *trans* isomers of compounds I-X, and differences in chemical shifts ($\Delta\delta$) between corresponding protons in *cis-trans* isomers, measured in CS₂ solution.

Benzo[<i>c</i>]phenanthrene series	Proton:	α, β	2'	3'	4	5	6	7	CH ₃ or CH ₂ X
I	<i>cis</i>	6.72			8.83	8.33	7.18		
	<i>trans</i>	7.23			8.96	9.00			
	$\Delta\delta$	0.51			0.13	0.67			
II	<i>cis</i>	6.84			8.78	8.06	6.44	7.20	
	<i>trans</i>	7.34			9.03	9.06	7.58		
	$\Delta\delta$	0.50			0.25	1.00	1.14		
III	<i>cis</i>	7.05			8.70	7.98	6.81	7.28	
	<i>trans</i>				9.06	9.03	7.61		
	$\Delta\delta$				0.36	1.05	0.80		
IV	<i>cis</i>				8.78	7.98	6.61	7.25	2.96
	<i>trans</i>				9.14	9.10			2.96
	$\Delta\delta$				0.36	1.12			0
V	<i>cis</i>	6.62	7.22	6.67	8.79	8.35			3.62
	<i>trans</i>	7.11	7.38	6.78	8.92	8.99			3.75
	$\Delta\delta$	0.49	0.16	0.11	0.13	0.64			0.13
VI	<i>cis</i>	6.73	7.25	7.14	8.79	8.26			4.49
	<i>trans</i>	7.21	7.42	7.27	8.97	9.02			4.57
	$\Delta\delta$	0.48	0.17	0.13	0.18	0.76			0.08

Table I (contd.)

Phenanthrene series	Proton:	α, β	2'	3'	4	5	6	7	CH ₃ or CH ₂ X
VII	<i>cis</i>	6.81			8.55	8.36			
	<i>trans</i>	7.36			8.71	8.74			
	$\Delta\delta$	0.55			0.16	0.38			
VIII	<i>cis</i>	6.94			8.62	8.38			
	<i>trans</i>	7.51			8.76	8.76			
	$\Delta\delta$	0.57			0.14	0.38			
IX	<i>cis</i>	7.02			8.66	8.42			
	<i>trans</i>	7.59			8.80	8.78			
	$\Delta\delta$	0.57			0.14	0.36			
X	<i>cis</i>	6.69, 6.86			8.41	8.21			
	<i>trans</i>				8.55	8.55			
	$\Delta\delta$				0.14	0.34			

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.

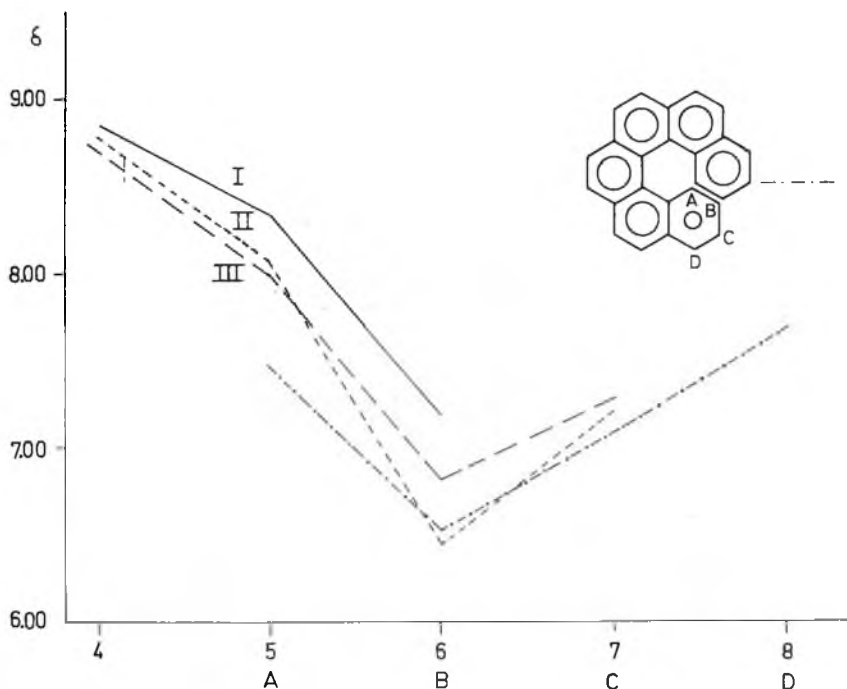


Fig. 1. δ values of corresponding protons in *cis* isomers I-III and hexahelicene.

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 δ -values for several protons in compounds I-IV, VII and VIII are given.

Table II

Temperature dependence of chemical shifts (ppm $10^2/^\circ\text{C}$) in CS_2 solutions between 25° and -70°C . (Negative values mean upfield shifts on lowering of temperature.)

	α, β		4		5		6		7	
	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>
I	-0.04	0	-0.11	-0.11	-0.23	-0.04	-0.10			
II	0.0	-0.02	-0.10	-0.11	-0.27	-0.06	-0.39		-0.06	
III	-0.02		-0.10	-0.18	-0.22	-0.06	-0.16			
IV	-0.03		+0.11		-0.33		-0.27			
VII*	-0.03		+0.01		+0.08					
VIII*	+0.03	+0.07	+0.05	+0.05	+0.13	+0.07				

* Measured in AsCl_3 .

Table III

Temperature-effect on chemical shift of protons in compound II, measured in different solvents (ppm $10^2/^\circ\text{C}$).

	α, β		4		5		6		7	
	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>
CS_2	0	-0.02	-0.10	-0.11	-0.27	-0.06	-0.39	-	-0.06	-
diglyme	+0.08	+0.02	-0.06	0	-0.26	0	-0.33	-	-0.02	-
DMSO	-0.05	-	-0.11	-0.07	-0.27	0.06	-0.36	-	-0.08	-

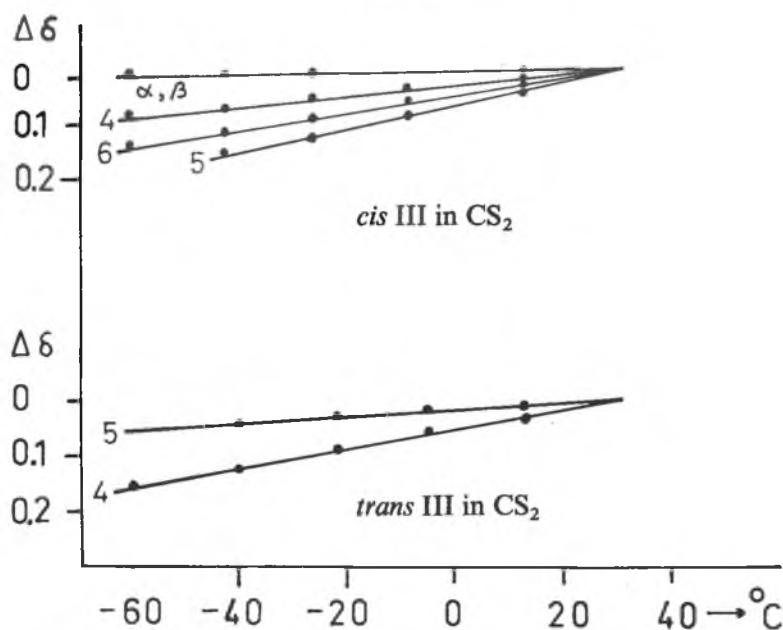


Fig. 2. Temperature effect on the chemical shifts of protons α , β , 4, 5 and 6 in *cis* and *trans* III ($\Delta\delta$ in ppm).

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 $10^2/^{\circ}\text{C}$); 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.

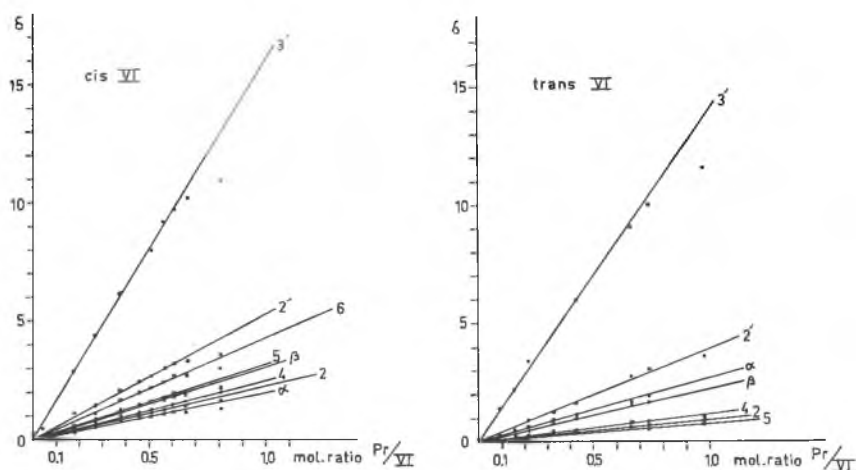


Fig. 3. Influence of the shift reagent $\text{Pr}(\text{DPM})_3$ on δ -values of protons in *cis* and *trans* VI (δ in ppm; solvent CS_2).

In Fig. 3 shifts of several protons in *cis* and *trans* VI are given in dependence on the mol. ratio $\text{Pr}(\text{DPM})_3/\text{VI}$. 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 .

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

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

* After completion of this investigation Prof. R. H. Martin informed us that he had drawn a similar conclusion. See: R. H. Martin, N. Defay, H. P. Figeys, K. Lè Van, J. J. Ruelle and J. J. Schurter, *Helv. Chim. Acta* 55, 2241 (1972).

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.

(Received December 1st, 1972)