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219. Studies in the Helicene Series
NMR. Evidence of 'Helicene-like' Conformations in the *cis* 1,2-Diarylethylenes

Part XVII[1])

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(26. VI. 72)

Summary. The *cis* and *trans* isomers of eight 1,2-diarylethylenes, precursors of helicenes, have been studied by NMR. spectroscopy. The observed differences in chemical shifts, specific solvent effects and steric effects (bromo derivatives) can be explained by the contribution of 'helicene-like' conformers in the *cis* isomers.

In the course of our work on the photosynthesis of helicenes, we have frequently observed that the NMR. spectra of the *cis*-1,2-diarylethylenes and of the corresponding helicenes show striking similarities[3]).

Independent and similar observations made by *Laarhoven et al.*[4]) prompt us to describe briefly some of our findings[5]).

1. The 1-aryl-2-(benzo [c] phenanthryl) ethylene series. – When the NMR. spectra of the *cis* isomers are compared to the NMR. spectra of the corresponding *trans* isomers (Table 1A), the following upfield shifts are observed, by first order analyses:

Ethylenic protons and H_1 (H_{a4} *ortho* to the side chain). Similar shifts were observed, long ago, in the NMR. spectra of *cis* versus *trans* stilbene [2].

A particularly large upfield shift in the case of H_{11} and H_{12} (except for H_{11} in **I**). This shielding increases according to the sequence: phenyl $<$ 3-phenanthryl $\simeq$ 2-benzo[*c*]phenanthryl $<$ 2-naphthyl.

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[1]) XVI see [1].

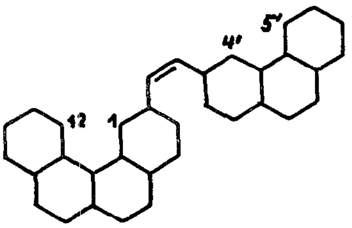
[2]) Author to whom correspondence should be addressed.

[3]) The main conclusion of this work is included in the PhD thesis of one of us (*J.J.S.*) presented 10 March 1972.

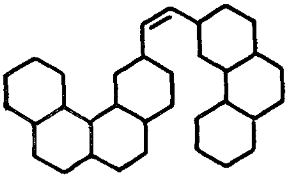
[4]) Private communication from Dr. *W. H. Laarhoven*, University of Nijmegen.

[5]) An X-ray diffraction study of *cis* 1-(2-benzo[*c*]phenanthryl)-2-(3-phenanthryl) ethylene is presently under way. Preliminary results show that the crystals belong to the $P2_1$ space group; personal communication from *G. Germain, H. Kagan, A. Moradpour, G. de Rango & M. Tsoucaris.*

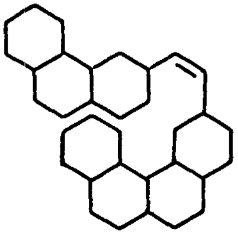
Two of the four 'extreme' conformations of the *cis* isomers, namely conformations **c** and **d**, show partial or complete overlap of benzene rings.



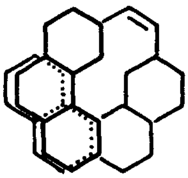
IIIa



IIIb



IIIc



IIId

If the contribution of conformers **c** and/or **d** is important, it is not surprising to find analogies between the NMR. spectra of the *cis*-1,2-diarylethylenes and of the corresponding helicenes. *It should however be strongly emphasised that there is* no *direct correlation between this observation and the ease of photocyclodehydrogenation to the helicene structures* (e.g., modification of the geometry in the excited state). Indeed, in the above sequence, the largest upfield shifts are observed in the case of *cis*-1-(2-benzo[*c*]phenanthryl)-2-(2-naphthyl)ethylene, which, contrary to the other 1,2-diarylethylenes (phenyl, 3-phenanthryl and 2-benzo[*c*]phenanthryl) does not give the helicene structure preferentially!

Small upfield shifts (*cis* versus *trans*) of the protons of rings C and D have been observed in 1,2-bis(2-benzo[*c*]phenanthryl)ethylene **IV** and in the substituted derivative **VII**[6]: H_{10} (ring D) in **IV** ($\Delta = 13$ Hz), H_7 (ring C) in **VII** ($\Delta = 6$ Hz). On the other hand, H_5 (ring B) in **VII** is unaffected ($\Delta = 0$).

The small phenyl radical in **VIII**[7]) has little influence on the protons of ring C.

Specific solvent effects. In our publication on the NMR. spectra of the helicenes [3], we have described a specific solvent effect ($CDCl_3/C_6D_6$) on the first protons of the helix. A similar specific solvent effect is observed in the case of the *cis*-1,2-diarylethylene **IV**: H_1 and H_{12} are shifted to low fields, H_{11} is not affected and the other protons are shifted to high fields (Table 2).

On the other hand, the *trans* isomer **IV** shows the selective solvent effect characteristic of the benzo[*c*]phenanthrene ring system.

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[6] *cis*-1-(6-methoxycarbonyl-2-benzo[*c*]phenanthryl)-2-(2-benzo[*c*]phenanthryl) ethylene (**VII**), H_5: 510 Hz, and H_7: 524 Hz.

[7] *cis*-1-(6-methoxycarbonyl-2-benzo[*c*]phenanthryl)-2-phenylethylene (**VIII**), H_5: 508 Hz ($\Delta_5 = 0$), and H_7: 526 Hz ($\Delta_7 = 2$).

Bromo derivatives. When a bromine atom is introduced in position 3 of the 2-benzo[*c*]phenanthryl system (**V** and **VI**), appreciably larger upfield shifts are observed. For steric reasons, the contribution of conformers **a** and/or **b** becomes smaller. With the view to further increase the contribution of conformer **d**, we are working on the synthesis of a dibromo-1,2-diarylethylene bearing one bromine atom, *ortho* to the side chain, in each of the two aryl radicals.

2. The 1-aryl-2-(3-phenanthryl)ethylene series. – In the phenanthryl radical of *cis*-**III**, H_5' is shifted to higher fields (*cis* versus *trans*). This upfield shift is, however, smaller than the upfield shift of the corresponding proton H_{12} ($H_{\alpha 4}$) in the benzo[*c*]phenanthrene system.

A similar effect is already observed in *cis*-**IX** and *cis*-**X**, two precursors of the pentahelicene skeleton (Table 1B).

Table 1. *Chemical shifts of the* cis-*1,2-diarylethylenes* (in $CDCl_3$) *and* $\Delta\delta$ trans-cis

A. *2-Benzo*[c]*phenanthryl radical and ethylenic protons*

$Ar—CH_\alpha=CH_\beta—Ar'$ a)			*cis:* δ (Hz at 60 MHz)				$\Delta = \delta_{trans}-\delta_{cis}$			
	Ar	Ar'	$H_{\alpha\beta}$	H_1	H_{12}	H_{11}	$\Delta_{\alpha\beta}$	Δ_1	Δ_{12}	Δ_{11} b)
I	④	①	406	536	504	>431	31	8	43	<26
II	④	②	416	537	490	390	33	15	62	67
III	④	③	417	539	500	401	32	10	49	56
IV c)	④	④	422	548	500	411	31	4	52	46
V	3-Br ④	①	410	526	472	422		31	69	35
VI	3-Br ④	②	416	521	<470	348		37	>71	109

B. *3-Phenanthryl radical and ethylenic protons*

	Ar	Ar'	$H_{\alpha\beta}$	H_4	H_5	$\Delta_{\alpha\beta}$	Δ_4	Δ_5
III	③	④	417	522	504	32	0	18
IX	③	4-$COOCH_3$ ①	407	512	503	35	10	19
X	③	4-Br ①	403	511	502		7	18
XI	2-Br ③	②	417	514	476		21	46

a) Ar: ① phenyl, ② 2-naphthyl, ③ 3-phenanthryl, ④ 2-benzo[*c*]phenanthryl.

b) In the *trans* derivatives, the protons H_{11} appear in the complex pattern of the other aromatic protons and have not yet been assigned. The Δ_{11} were therefore deduced using the chemical shift of H_{11} in benzo[*c*]phenanthrene (457 Hz).

c) H_{10} 440 Hz ($\Delta = 13$).

Table 2. *Specific solvent effects:* $\delta_{CDCl_3} - \delta_{C_6D_6}$ (Hz at 60 MHz)

	IV *cis*	IV *trans*		[7] helicene	benzo [*c*] phenanthrene
H_1	– 9	0			
H_{12}	–14	0	H_1	–15	+ 1
H_{11}	0		H_2	0	+15
other protons	+13	+14	other protons	+ 5 to +11	+12

Because of the presence of the bromine atom in *cis*-1-(2-bromo-3-phenanthryl)-2-(2-naphthyl)ethylene (**XI**), the upfield shift of H_5 ($H_{\alpha 3}$) is much larger than in the corresponding unsubstituted *cis*-1,2-diarylethylene.

We acknowledge the fact that other co-workers have made similar observations in the course of the last few years. The financial support of the *'Fonds de la Recherche Fondamentale Collective'* is gratefully acknowledged. One of us (*J.J.R.*) expresses his gratitude to the *'Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture'* for the award of a fellowship.

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220. Reaction of 2-Methylenenorbornane with N-Bromosuccinimide

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Summary. The reaction of 2-methylenenorbornane with N-bromosuccinimide produced a mixture of six monobromides in an overall yield of about 60%. By irradiation in the presence of benzoyl peroxide *exo*- and *endo*-3-bromo-2-methylenenorbornanes, 2-bromomethylnorborn-2-ene, *Z*- and *E*-2-bromomethylenenorbornanes and 1-bromomethylnortricyclene were found in a percentage ratio of 43.0, 7.5, 6.5, 19.0, 19.0 and 5.0. Without benzoyl peroxide, in the dark, the same products were obtained, but in a percentage ratio of 23.0, 3.0, 17.0, 26.0, 26.0 and 7.0. These results are rationalized in terms of an ionic mechanism in concurrence with some radical mechanism contribution.

Introduction. – The use of N-bromosuccinimide (NBS.) as a reagent for the allylic bromination of olefins is a standard preparative procedure [1]. In general it is thought that the mechanism involves intermediate formation of the free allylic radical which subsequently captures bromine [2]; however, alternative mechanisms have been proposed. A variant of the radical mechanism is that a chain process occurs on the surface of the NBS. [3]. An older suggestion is that the reagent responsible is molecular bromine formed in low concentrations by decomposition of NBS. [4]. However, if the concentration of bromine is allowed to increase, addition to the double bond occurs and thus the course of the reaction can deviate [5]. This diversion becomes the major route for those molecules where a resonance-stabilized allylic radical is forbidden for structural reasons, as exemplified by norbornene and bicyclo[2.2.2]oct-2-ene. In both cases the products obtained can be satisfactorily rationalized in terms of the initial formation of a bromonium ion [6]. Even with 2-methylnorborn-2-ene (**1**) which has an allylic position available, it appears that an ionic mechanism best accounts for the major products [7]. The reaction of **1** with NBS. in boiling carbon tetrachloride with benzoyl peroxide in the light gave *exo*-3-bromo-2-methylenenorbornane (**2**) and