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Carbon-13 NMR Spectra of Isomeric Diazaphenanthrenes, II[1]
δ-Effects in Sterically Crowded Methyl Derivatives

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Steric downfield shifts due to a δ-CH moiety and a δ-nitrogen lone pair are similar in methylated diazaphenanthrenes. Most probably steric distortions are responsible for the δ-effects observed, and this might be quoted as a further evidence for a nearly equal steric requirement of a hydrogen atom and a nitrogen lone pair.

(Keywords: Carbon-13 NMR; Diazaphenanthrenes; Steric shifts)

C-13 NMR-Spektren isomerer Diazaphenanthrene, II[1]*. δ-Effekte in sterisch gehinderten Methylderivaten*

Sterisch bedingte Tieffeldverschiebungen infolge von δ-CH-Molekülteilen und δ-lone pairs von Stickstoffatomen sind in methylierten Diazaphenanthrenen ähnlich. Die gemessenen δ-Effekte dürften auf sterische Deformationen zurückzuführen sein, was als weiteres Indiz für den nahezu gleichgroßen Raumbedarf eines Wasserstoffatoms und eines freien Elektronenpaars am Stickstoff gewertet werden kann.

Introduction

A comprehensive review concerning effects governing C-13 shielding in aromatic compounds recently has been given by *Hansen*[2]. Besides the generally accepted relationship between $\delta\,^{13}C$ and the charge density at the carbon in question[3–5] several other effects were shown to be of importance, namely steric and dielectric field (DEF) effects[2]. This appears to be one of the main reasons for several fair correlations between $\delta\,^{13}C$ and charge density, especially with methyl derivatives[6].

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Among the effects not clearly accounted for by standard MO calculations are primarily peri-effects (so-called γ-upfield shifts in aliphatics) and δ-effects.

In the heteroaromatic series hitherto only peri-effects have been studied with methylated quinolines and isoquinolines[7], the data obtained compare favourably with corresponding data of the carbocyclic naphthalenes[8]. At present no data are available concerning δ-effects in methylated heteroaromatics.

As a continuation of our previous work on the C-13 NMR spectra of parent diazaphenanthrenes (*DAP*'s)[1] we investigated a variety of methylated derivatives.

Table 1. *Carbon-13 chemical shifts and methyl SCS of some methylated diazaphenanthrenes*

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-8	C-9	C-10	Me
1,7-*DAP*	—	148.9	121.9$_5$	135.3	128.6	128.6	150.7	121.4	132.3	—
(**1**) 10-Me-1,7-*DAP*	—	147.8	121.0	135.4	129.0	129.8	149.7	125.6	148.5	26.4$_5$
		-1.1	-0.9_5	0.1	0.4	1.2	-1.0	4.2	16.2	
(**3**) 8-Me-1,7-*DAP*	—	149.1	121.8	135.7	128.7	128.6	160.0	122.4	132.6	25.2
		0.2	-0.1_5	0.4	0.1	0.0	9.3	1.0	0.3	
4,7-*DAP*	131.9	121.5	150.2	—	130.3	130.3	150.2	121.5	131.9	—
(**2**) 1-Me-4,7-*DAP*	144.9	125.5	149.0	—	133.0	132.0	149.0	120.5	134.7	26.1
	13.0	4.0	-1.2		2.7	1.7	-1.2	-1.0	2.8	
(**4**) 2-Me-4,7-*DAP*	130.8	131.3	151.7	—	130.4	129.8	150.0	121.3	131.7	18.8
	-1.1	9.8	1.5		0.1	-0.5	-0.2	-0.2	-0.2	

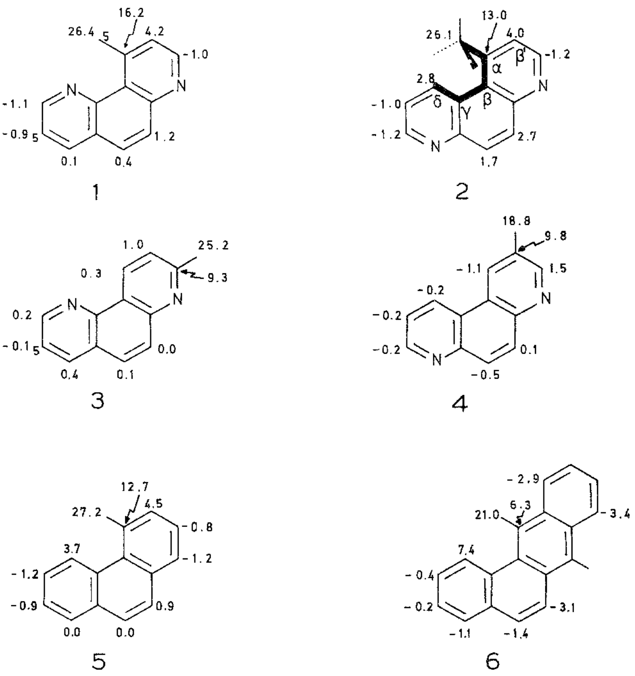
Results and Discussion

In Scheme **1** the methyl substituent chemical shifts (SCS), defined as δC_i (methyl *DAP*) — δC_i (parent *DAP*)[1], are given for 10-methyl-1,7-*DAP* (**1**), 1-methyl-4,7-*DAP* (**2**), 8-methyl-1,7-*DAP* (**3**), and 2-methyl-4,7-*DAP* (**4**) along with the data for 4-methylphenanthrene (**5**)[9] and 7,12-dimethylbenz[a]anthracene (**6**)[10] for comparison.

The relevant chemical shifts are compiled in Table 1, a comparison of the data should be facilitated by the graphs of Scheme **1**.

Usual methyl SCS[7] were found for compounds **3** and **4**, but as noted for methylated polycyclic aromatics[6,8,11], the methyl substitution slightly perturbs nearly all carbon shifts of the molecule (because of ambiguities in assignment of the quaternary carbon shifts these data were omitted in Scheme and Table 1). The methyl SCS measured for **1** and **2**, i.e. *DAP*'s with a sterically crowded methyl group, strongly deviate from values predicted by simple additivity. For a methyl group

Scheme 1



γ to a nitrogen one would expect, from measurements of other methylated *DAP*'s devoid of such a steric situation*, 8.4_5 ppm for the methyl bearing carbon and the methyl resonance at 18.7 ppm. Thus, the excessive downfield shifts for **1** and **2** are 7.7_5 and 4.5_5, and 7.7_5 and 7.4 ppm, respectively. These data agree very well with those of compound **5** with a methyl group in a similar spatial arrangement. It should be noted that the reference *DAP*'s with a methyl group γ to a nitrogen atom always show a peri-shift, but the data of the unperturbed 4-methylpyridine are not strikingly different[12].

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* A total of 14 methylated *DAP*'s has been studied.

The carbons in δ-orientation with respect to the methyl group are found to be deshielded by 2.8 (**2**), 3.7 (**5**), and 7.4 (**6**) ppm. The downfield shifts noted for the carbons of the δ-fragment (thick line in formula **2** in Scheme 1) are comparable with δ-effects observed in a variety of aliphatics[13], but there the penultimate carbons mostly suffering the largest deshielding.

Interestingly, the replacement of the δ-CH moiety of **2** by a nitrogen lone pair in **1** results in similar δ-effects for both the methyl and the methyl bearing α-carbon resonances.

In our opinion this is primarily due the comparable steric requirement of a hydrogen atom and a nitrogen lone pair[14] rather than anisotropic effects excerted by the lone pair because anisotropic shifts are of the same order of magnitude in ^{13}C and ^{1}H NMR with maximum values of about 1.5 ppm. A similar problem represents the separation of steric and DEF effects of polar substituents[2].

A T_1 study on **6** revealed that the 12-methyl group is very slowly rotating due to a twofold γ- and δ-steric interaction with neighboured protons[15], the main contribution was thought to arise from the very short distance, about 4 nm, between the "locked methyl"[8] and the δ-CH moiety. Because of the structural similarity between **6** and **1**, **2**, and **5** the same steric effects may be operating resulting in comparable shift changes, and conclusively the preferred conformations of the methyls should be, as shown for **2**, P_{21} as proposed for **6**[8]. Due to close proximity of the ultimate carbons sterically caused bond angle deformations (decreased methyl-Cα-Cβ′ bond angle) are most probably responsible for the δ-effects observed in aromatics and heteroaromatics, which are opposite in sign to γ-effects. Therefore the CH-polarization model proposed for the latter[16] fails in predicting δ-effects. On the contrary, γ- and δ-effects have been explained in terms of bond and torsion angle changes for conformationally more flexible aliphatics[17]. In our case deformations also may account for the observed excessive deshielding of the β′-positions (3.1 and 2.9 ppm for **1** and **2**) as a consequence of a shortened distance between methyl and β′-CH protons. Introduction of substituents at C-8 into 1-substituted naphthalenes is accompanied by similar deshieldings of C-2 and C-7[6,18].

In general, the terminal carbons in γ-arrangements are shielded and adjacent protons deshielded in agreement with the CH-polarization model[16], but the short distant δ-interactions move both proton *and* carbon resonances downfield. This unusual fact also might be quoted as additional evidence for bond angle deformations associated with δ-effects.

Experimental

Compounds **1**-**4** were prepared as described previously[19]. Carbon-13 NMR spectra were run on a Jeol JNM-PS 100 PFT instrument operating at 25.15 MHz. Sample solutions were 0.8-1.1 *M* in $CDCl_3$ with added *TMS* as internal reference. A 4K computer memory was used at a sweep width of about 5 kHz resulting in an accuracy of the chemical shifts of about ± 0.15 ppm.

Assignments were made as described for parent *DAP*'s[1] with the aid of the data of several methylated azines.

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