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CONJUGATION IN MACROCYCLIC BOND SYSTEMS—VI[1]

'H-CHEMICAL SHIFTS OF ANNELATED ANNULENES

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Abstract—The nonlocal contribution of the pi-electrons to the 'H-chemical shifts in the annulenoid systems **1**–**12** is calculated within the HMO theory from which information is gained about the change of the annulenoid character of (4n) and (4n + 2)-annulenes by different annelated groups. The predicted trends are then compared with experimental data. Calculated ground state stabilization energies and aromaticity indices based on the uniformization of bond lengths show no correlation with the chemical shifts.

INTRODUCTION

Annulenes with (4n + 2) pi-electrons are diatropic whereas those with (4n) pi-electrons are paratropic[2-4] and their magnetic properties are changed by substituents or annelated groups. To study these changes we calculated the 'H-chemical shifts of the [12] and [14] annulenes shown in Fig. 1. Our calculations on other possible isomers of **4**–**6** and **8**–**12** are not reported here since the results are very similar to those in the present paper.

We used the modified HMO theory of Roberts[5] with the following parameters: The coulomb integrals $\alpha_C = 0$, $\alpha_O = 2.5$ and the resonance integrals $\beta_{CC} = 1$, $\beta_{CO} = 0.8$. Since experimental geometries are only known for **7** we used "ideal" geometries, i.e. all C–C and C–O bondlengths were fixed at 1.4 Å, C–H at 1.08 Å and bondangles at 120°. The introduction of bond alternation will reduce the diatropic or paratropic effects. It is, however, uncertain which degree of alternation may be appropriate. Therefore bond alternation was not taken into account. The paratropic effects of annulenes with (4n) pi-electrons will be much more reduced by bond alternation than the diatropic effects of annulenes with (4n + 2) pi-electrons.[2] The calculated 'H-chemical shifts δ (in ppm, δ: =0 for TMS, δ > 0 for upfield shifts) are absolutely too large and therefore only of qualitative nature. The inner protons are always calculated at too high a field since the strong nonbonded interaction between them will cause deshielding.[6]

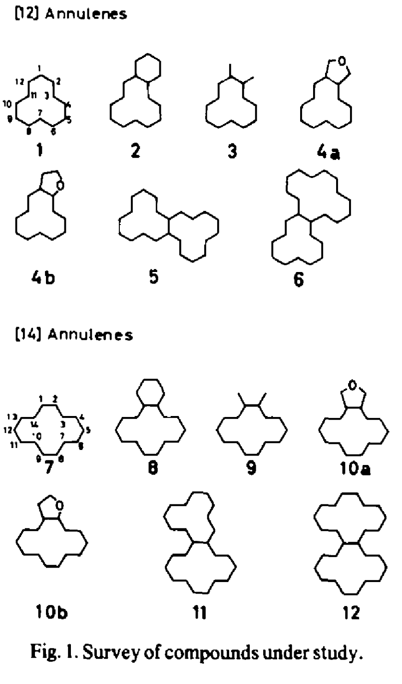

Fig. 1. Survey of compounds under study.

'H-*Chemical shifts*

In all the [12]annulenes resp. [14]annulenes the atoms are numbered in the same manner as **1** or **7** in Fig. 1. Starting with number 13 or 15 the atoms of the annelated groups are numbered clockwise as in the annulene part. The compounds **2'**, **4'**–**6'**, **8'**, **10'**–**12'** correspond to **2**, **4**–**6**, **8**, **10**–**12** but the bond which is common to the annulene and the annelated group is now deleted. The calculated 'H-chemical shifts are given in the Tables 1–3. The mean

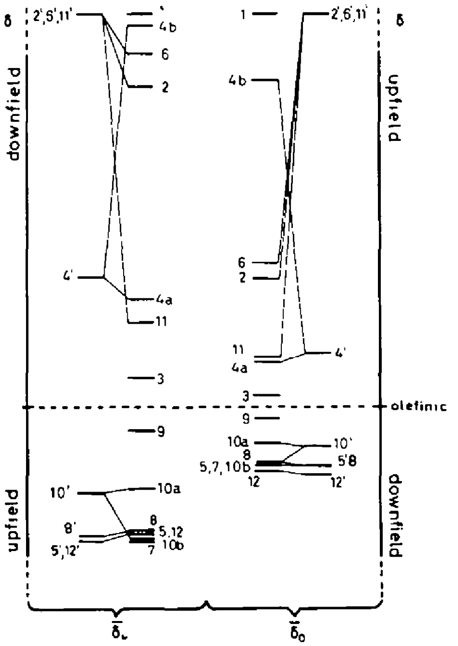

Fig. 2. Mean chemical shifts $\bar{\delta}_i$ and $\bar{\delta}_o$ of **1**–**12** and **2'**, **4'**–**6'**, **8'**, **10'**–**12'**. The chosen scale is $|\delta - \delta_0|^{0.7} \cdot \delta/|\delta|$ where $\delta_0 = -5.79$ is the theoretical value of an olefinic proton. Infinite values have been put to the ends of the scale.

Table 1. Calculated ^{1}H-chemical shifts δ (in ppm) of the [12]annulenes

	[12]Annulenes						
	1[a]	**2**	**3**	**4a**	**4b**	**5**	**6**
Proton		benzene	dimethylene	[c]furan	[b]furan	[12]annulene	[14]annulene
3	$-\infty$	−43.2	−6.98	−13.1	−151.0	+4.13	−48.7
7		−43.4	−6.98	−14.2	−151.0	+4.28	−49.0
11		−43.3	−6.98	−14.2	−151.0	+4.37	−48.9
$\bar{\delta}_i$[b]		−43.3	−7.0	−13.8	−151.0	+4.3	−48.9
1	$+\infty$					−8.60	
2						−10.1	
4		+4.86	−5.47	−3.41	+34.2		+7.17
5		+3.55	−5.50	−3.70	+29.9		+5.04
6		+4.53	−5.47	−3.48	+33.7	−9.29	+6.12
8		+4.52	−5.47	−3.48	+33.7	−8.84	+6.10
9		+3.51	−5.50	−3.71	+29.8	−8.46	+4.93
10		+4.59	−5.47	−3.46	+33.8	−8.75	+6.20
12		+4.98	−5.47	−3.35	+34.5	−8.78	+6.77
$\bar{\delta}_0$[b]		+4.4	−5.5	−3.5	+32.8	−9.0	+6.0
13		−0.96	−5.72[c]	−4.50	+7.43		[d]
14		−2.28	−5.70[c]	−4.37	+3.50		
15		−2.18					
16		−0.03					

[a] HOMO and LUMO are degenerate.

[b] $\bar{\delta}_{i(o)}$ is the mean value of the inner (outer) protons.

[c] Both methylene protons have the same δ value.

[d] The protons 13–24 of **6** correspond to the protons 3–14 of **11** (cf. Table 2).

Table 2. Calculated ^{1}H-chemical shifts δ (in ppm) of the [14]annulenes

	[14]Annulenes						
	7	**8**	**9**	**10a**	**10b**	**11**	**12**
Proton		benzene	dimethylene	[c]furan	[b]furan	[12]annulene	[14]annulene
3	+5.20	+3.78	−4.85	−0.54	+4.75	−10.9	+4.55
7	+5.20	+3.94	−4.85	−0.46	+4.81	−11.8	+4.26
10	+5.20	+3.94	−4.85	−0.46	+4.81	−11.7	+4.26
14	+5.20	+3.78	−4.85	−0.54	+4.75	−10.7	+4.55
$\bar{\delta}_i$[a]	+5.2	+3.9	−4.9	−0.5	+4.8	−11.3	+4.4
1	−9.23						−9.34
2	−9.23						−9.34
4	−9.14	−9.15	−6.08	−7.59	−9.12	−1.25	−9.29
5	−8.79	−8.59	−6.05	−7.32	−8.72	−3.10	−9.06
6	−9.14	−8.88	−6.08	−7.48	−9.06	−3.04	−10.7
8	−9.23	−8.95	−6.09	−7.52	−9.14	−3.03	
9	−9.23	−8.95	−6.09	−7.52	−9.14	−3.01	
11	−9.14	−8.88	−6.08	−7.48	−9.06	−2.95	−10.7
12	−8.79	−8.59	−6.05	−7.32	−8.72	−2.78	−9.06
13	−9.14	−9.15	−6.08	−7.59	−9.12	+2.25	−9.29
$\bar{\delta}_0$[a]	−9.1	−8.9	−6.1	−7.5	−9.0	−2.1	−9.6
			−5.88				
15		−8.88	−5.67	−7.58	−7.47	[b]	
			−5.88				
16		−8.23	−5.87	−7.58	−6.98		
17		−8.23					
18		−8.88					

[a] $\bar{\delta}_{i(o)}$ is the mean value of the inner (outer) protons.

[b] The protons 15–24 of **11** correspond to the protons 3–12 of **6** (cf. Table 1).

values of the inner ($\bar{\delta}_i$) and outer ($\bar{\delta}_0$) protons of the considered annulene part can be used for comparing the different compounds (cf. Fig. 2). The annelated groups reduce the ring current in the order:

[b]Furan < [14]annulene < benzene < [c]furan < dimethylene < [12]annulene. This order applies to the inner protons of the [12] and the [14]annulenes as well as to the outer protons of [12]annulenes. The [b]furan- and the [14]annulene-groups are exchanged for the outer protons of the [14]annulene (cf. Table 2). The order of the "small" annelated groups [b]furan, benzene, [c]furan and dimethylene follows closely the bond order of the bond which is common to the annulene and the annelated group (cf. Table 4). The yet unknown compounds **3** and **9** are calculated to be almost olefinic which corresponds to the fact that radialenes are described as nonaromatic.[7] The

Table 3. Calculated ^{1}H-chemical shifts $\bar{\delta}_{i(o)}$ (mean values of the inner (outer) protons) of **2′**, **4′–6′**, **8′**, **10′–12′**

Compound	$\bar{\delta}_i$	$\bar{\delta}_o$
2′[a]	$-\infty$	$+\infty$
4a′, **4b′**	−16.1	−2.9
5′	+5.1	−9.1
6′[a]	$-\infty$	$+\infty$
8′	+4.5	−9.1
10a′, **10b′**	−0.1	−7.6
11′[a]	$-\infty$	$+\infty$
12′	+5.2	−9.9

[a] HOMO and LUMO are degenerate.

Table 4. The bond orders P of the bond which is common to the annulene and the annelated group of **1–12**

	[12]Annulenes		[14]Annulenes	
Annelated group	Compound	P	Compound	P
	1[a]	0.622	**7**	0.642
Benzene	**2**	0.546	**8**	0.502
Dimethylene	**3**	0.357	**9**	0.366
[c]Furan	**4a**	0.425	**10a**	0.419
[b]Furan	**4b**	0.663	**10b**	0.564
[12]Annulene	**5**	0.331	**11**	0.491
[14]Annulene	**6**	0.491	**12**	0.473

[a] HOMO and LUMO have been singly occupied.

Table 5. Experimental ^{1}H-chemical shifts δ (in ppm) of the dimethylmonodehydro[12]annulenes **13–16** and the dimethylbisdehydro[14]annulenes **17–21** (cf. Fig. 3)

Compound	H^C	$H^{C'}$	H^X	H^Y	Ref.
[12]Annulenes:					[8a]
13, Alkyl	−5.73				
14, [b]Furan	−5.80	−5.91	−6.06	−7.09	
15, Benzene	−6.10		−7.08	−7.08	
16, [c]Furan	−6.28		−7.21		
[14]Annulenes:					
17, Alkyl	−8.24				[8b]
18, [b]Furan	−7.77	−7.77	−7.24	−7.78	
19, Benzene[a]	−7.08		−8.25	−7.51	[9]
20, [c]Furan	−6.72		−7.82		[10]
21, [14]Annulene	−7.31				[11]

[a] The corresponding benzo[14]annulene has been synthesized by H. A. Staab.[15] Since this compound is the only one in the series **7–12** we used the dehydro[14]annulenes **17–21** for for comparison.

differences in the chemical shifts between **5**, **8**, **10a**, **12** and the corresponding monocyclic compounds **5′**, **8′**, **10a′**, **12′** are very small. Therefore the compounds **5**, **8**, **10a** and **12** can be regarded as only small perturbed annulenes **5′**, **8′**, **10a′** and **12′**.

The above stated order of the annelated groups agrees well with that found for the external proton H^C of the monodehydro[12]annulenes **13–16**[8a] and of the bisdehydro[14]annulenes **17–21**[8b–11] (cf. Fig. 3 and Table 5). The experimental chemical shifts of the inner protons of **13–21** cannot be compared with our calculated values since the *trans* double bonds in these compounds might be conformationally mobile.[8–11] It might also be possible that the inner protons are influenced by the anisotropies of the triple bonds. The chemical shifts of the protons at the annelated groups are strongly affected by the electronic structure of the annulene part (cf. Ref.[12]). Fusion of a (4n) resp. (4n + 2) pi-electron system shifts the benzene and furan proton resonances to higher or lower field as is shown by our calculations (cf. Table 1 and 2) as well as by experiment (cf. Table 5). We wish to emphasize that especially benzene fused to annulenes can give information about the extent of bond alternation in the annulene part since the chosen method is parametrized to reproduce correctly the chemical shifts of benzenoid hydrocarbons. Our calculations support the assignment of H^X and H^Y in dimethylbenzobisdehydro[14]annulene **19**.[9] The protons H^X and H^Y of dimethylbenzomonodehydro[12]annulene **15** have the same chemical shift.[8a] Therefore we can conclude that in the [12]annulene **15** double bond fixation is more important than in the corresponding [14]annulene **19**.

We also calculated the aromaticity indices, A, of Julg[13] which are based on the uniformization of the bondorders of the peripheral bonds and the homodesmotic stabilization energies[14] considering only pi-energy differences. No correlations were found between the ground state stabilization energies and either the mean chemical shifts or the aromaticity indices.

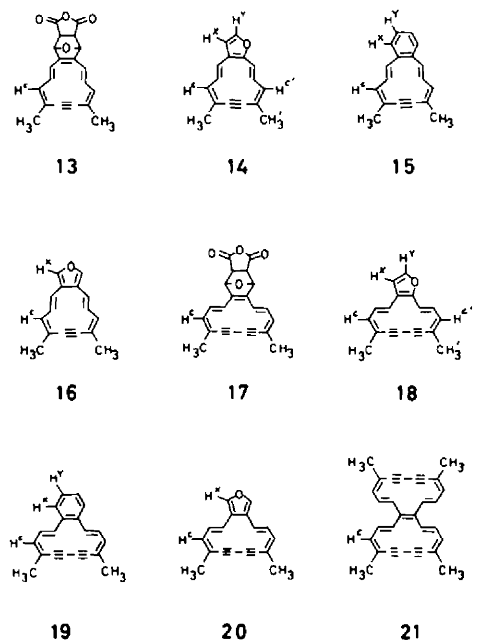

Fig. 3. Survey of known monodehydro[12]annulenes and bisdehydro[14]annulenes.

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