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^{1}H-CHEMICAL SHIFTS OF SOME DEHYDRO[12]- AND DEHYDRO[14]-ANNULENES*

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Abstract—The ring-current (RC) and local anisotropic (LA) contributions to the ^{1}H-chemical shifts of the dehydro[12]- and dehydro[14]-annulenes 1–13 have been calculated. The calculated shifts are in very good accord with experiment. Only protons with distances <3 Å from a triple bond are obtained at too high a field. It is shown that only the consideration of the combined RC and LA effects can provide an explanation of the chemical shifts of inner and outer protons of annulenes.

INTRODUCTION

Annulenes with $(4n+2)$ π-electrons are diatropic whereas those with $(4n)$ π-electrons are paratropic.[1-3] In a previous paper[4] we studied the ^{1}H-chemical shifts of [12]- and [14]-annulenes by means of HMO calculations. There only the ring current (RC) contributions to the chemical shift have been taken into consideration and it was only possible to derive qualitative conclusions. Recently it was shown[5] by applying a classical model that local anisotropic (LA) contributions are as important as RC effects. Therefore, we developed a quantum mechanical theory[6] which allows one to calculate the RC and the LA contributions of the π- and σ-electron systems within the framework of an extended π-theory.[7] This theory is applicable to any planar conjugated hydrocarbon containing sp^2- and sp-hybridized carbon atoms. For the first time it is then possible to calculate chemical shifts of macrocyclic dehydroannulenes with triple and cumulated double bonds. In dehydroannulenes the conformative mobility is smaller as compared with annulenes with only sp^2-hybridized atoms. This fact facilitates the comparison of experimental and calculated shifts.

The compounds studied in this paper are shown in Fig. 1. All bondlengths were obtained by the self-consistent resonance integral procedure[6] starting with standard values (see Table 1). The symmetrical structures of **9**, **10** and **13** have been obtained starting with lower symmetry. All bond angles at sp-hybridized carbon atoms have been fixed at 180°; those at sp^2-hybridized atoms have been determined so that the deviations from 120° became minimal.[8] The C–H bondlengths have been fixed at 1.08 Å. All compounds were taken as planar. This assumption is justified, as was shown in the case of 3.[9]

The ^{1}H-chemical shift δ (in ppm, $\delta := 0$ for TMS, $\delta > 0$

Table 1. Standard and calculated bondlengths of the studied dehydro [12]- and [14] annulenes

		Bondlengths/Å	
Bond	Standard[7,12]	Dehydro[12]annulenes	Dehydro[14]annulenes
$-C\equiv C-$	1.201	1.216 ± 0.001^d	1.226 ± 0.002^b
			$1.238 \pm 0.002^{c,e}$
$=C=C=$	1.280		1.249 ± 0.003^b
$=C=C<$	1.380		1.357 ± 0.008^b
			1.379 ± 0.005^c
$>C=C<$	1.335	1.353 ± 0.002	1.377 ± 0.005^b
			1.407 ± 0.012^c
$>C=C<$ [a]	1.397	1.414 ± 0.001	1.417 ± 0.004^b
			1.423^c
$\equiv C-C\leqq$	1.450	1.424 ± 0.005	1.403 ± 0.008^b
$\geqq C-C\leqq$	1.460	1.468 ± 0.006	1.437 ± 0.010^b

[a] Bond which is common to the annulene and the annelated group.

[b] Unsymmetrical dehydro[14]annulenes **11** and **12**.

[c] Symmetrical dehydro[14]annulenes **9**, **10** and **13**.

[d] Experimental value of the tribenzoderivative of **1** 1.192 Å, cf. Ref.[14].

[e] Experimental value of **9** 1.208 Å, cf. Ref.[15].

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*Dedicated to Professor O. E. Polansky on the occasion of his 60th birthday.

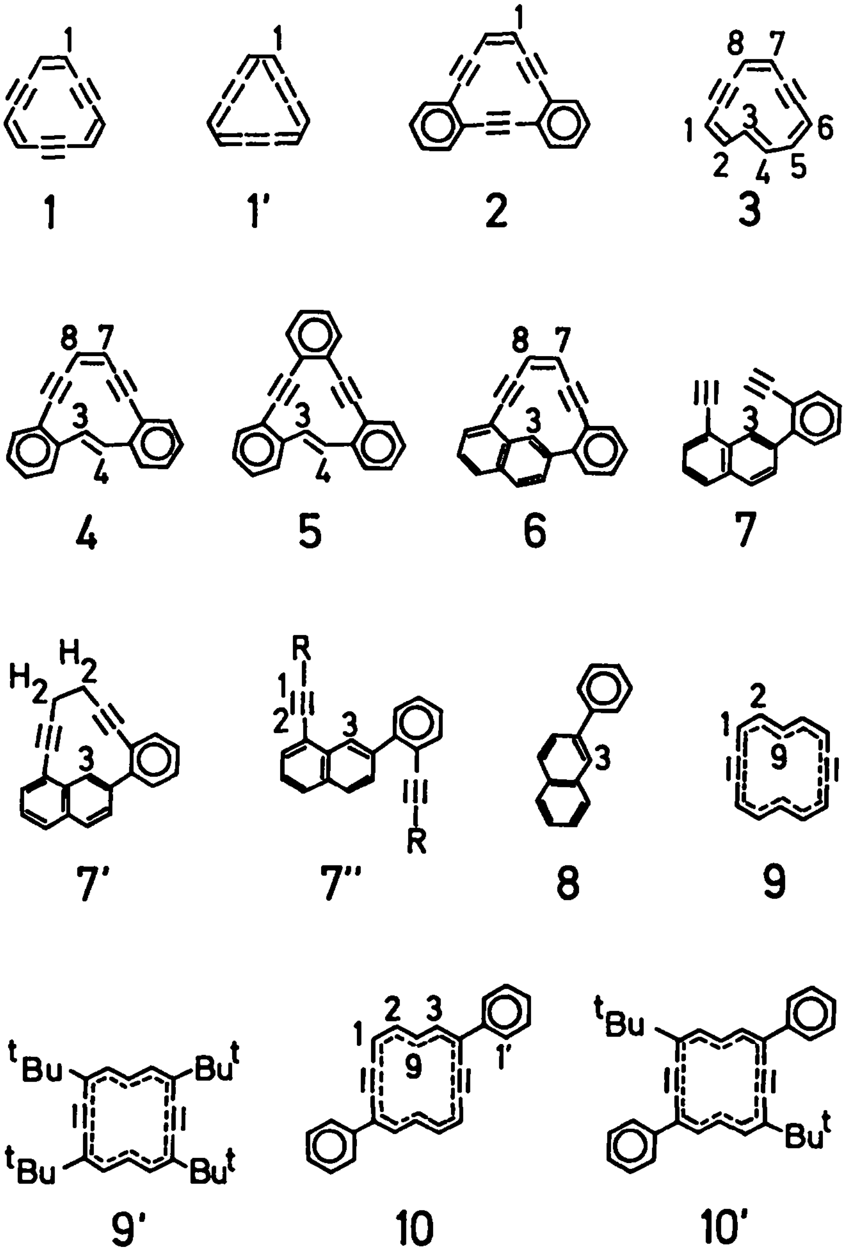


Fig. 1. Survey of compounds under study.

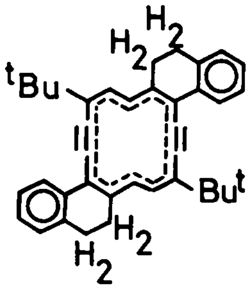
for downfield shifts) can be calculated in two ways:[6] $\delta_1 = \delta^{RC} + \delta^0$ taking into account only the RC contribution and $\delta_2 = \delta^{RC} + \delta^{LA} + \delta^0$ with the RC and LA effects. δ^0 defines the zero of the δ-scale. The π'-electron system spanned by the sp-hybridized atoms in the plane of the molecule does not contribute to δ^{RC}. δ^{LA} contains the LA effects of the π- and the π'-electron systems as well as of the σ-core which is taken as totally localized and unpolarizable. With all studied compounds the π-charge densities do not differ significantly from 1. Therefore, net charge contributions δ^q to the chemical shift are negligible. The experimental and calculated ^{1}H-chemical shifts are given in Table 2.

RESULTS AND DISCUSSION

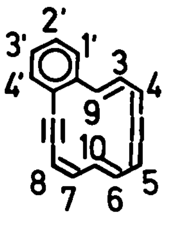
RC effects are considerably reduced with increasing localization of double and triple bonds.[1] We see in Table 1 that the multiple bonds are shorter in the [12]- than in the [14]-annulenes. Consequently the absolute δ^{RC} values of the compounds **1**–**6** are generally smaller than those of **9**–**13**. Also the unsymmetrical [14] annulenes **11** and **12** have shorter double and triple bonds and hence smaller $|\delta^{RC}|$ values than the symmetrical [14] annulenes **9**, **10** and **13**. The calculated triple bonds are, however, somewhat too long since we have neglected any interaction between the σ-core and the π'-electron system[7] (see Table 1). δ^{LA} is of the same order of magnitude leading to a downfield shift for nearly all protons. The absolute values of δ^{RC} and δ^{LA} of the outer protons of the [12] annulenes **1**–**5** are comparable in size. Both cancel since δ^{RC} has the opposite sign of δ^{LA} and we obtain shifts typical for olefinic protons. This shows that it is not correct to postulate the absence of a ring current in a cyclic conjugated hydrocarbon if the resonance lies in the range of olefinic protons. The downfield shift of the inner protons of the [12] annulenes results from the δ^{RC} and the δ^{LA} contributions. The same is valid for the outer protons of the [14] annulenes. δ^{LA} reduces the highfield shifts of the inner protons caused by the RC effect. The consideration of δ^{RC} alone would result in too extreme a shift, especially for the outer protons of [12] and the inner protons of [14] annulenes. On the contrary δ^{LA} could not give a useful explanation of the chemical shifts in the studied annulenes.

Let us now consider the experimental and calculated shifts in detail. In agreement with energetic arguments[9] we can conclude from the comparison of experimental and calculated shifts that 1 does not have the valence structure 1'. With the compounds 3, 4 and 5 only mean values are measured for the protons at the trans-double bond (see Refs. 9, 10). The mean deviation between calculated δ_2 and experimental δ values is only 0.25 ppm if we exclude all protons in direct proximity to a triple bond. With the exception of the protons H_7/H_8 of 6 the maximal error is ~0.5 ppm. This is a very good agreement between experimental and calculated shifts if we consider that the experimental values are "exact" only to within ~0.3 ppm as can be seen by inspection of their solvent and temperature dependence. It is interesting to note that the introduction of t-butyl substituents in 9 yields a downfield shift of ~1 ppm for the inner proton. Uncertainties in the chosen geometries might also result in errors up to 0.1–0.3 ppm in the calculated values.

The protons $H_{1'}$ of 10, $H_{3'}$ of 12 and 13, and $H_{4'}$ of 12 are calculated at too high a field. The error is ~0.5 ppm in the case of $H_{1'}$ of 10'' and $H_{4'}$ of 12' which have both fixed the phenyl substituent in the same manner. The same is true for $H_{3'}$ of 12' and 13' where the error amounts to 0.99 and 1.35 ppm. For $H_{1'}$ of 10' the error is reduced to 0.3 ppm. Since all other outer protons are reproduced very well, these additional downfield shifts cannot be explained by an under- or overestimation of the RC effect. All these protons have distances <3 Å from the middle of a triple bond. Therefore, we have to attribute this additional downfield shift to a special LA effect of the triple bond which is not taken into account in our theory. Possibly this effect is caused by charge density changes in the σ-core which we have totally neglected.[6] Then it is easy to understand that we find the greatest error for $H_{3'}$ of 12' and 13' since here the proton is in the same plane as the adjacent triple bond. $H_{4'}$ of 12' and $H_{1'}$ of 10'' might be a little distorted from this plane and the phenyl substituent of 10' is able to rotate freely thus reducing the distance from the triple bond. The inner protons of the [12] annulenes 3–5 are also calculated at too high a field. The inner proton of 6 is calculated 2.7 ppm at too high a field. Also H_3 of the noncyclic conjugated compound 7' is obtained 2.4 ppm at



10''



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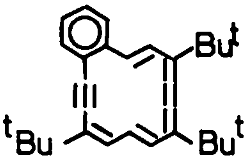
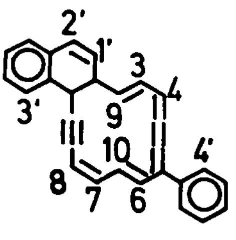


11'



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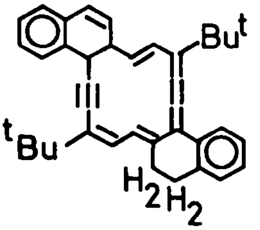
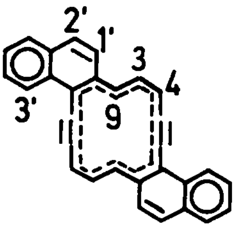


12'



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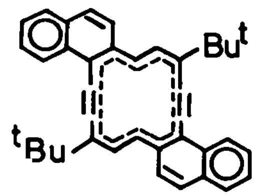
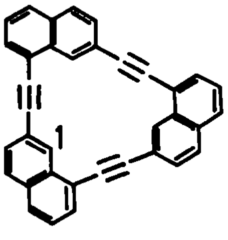


13'



14

too high a field, whereas in 8 it is correctly reproduced. By variation of the substituent R in 7″ we can see that these downfield shifts are caused indeed by charge density changes (see Table 3) in the triple bond. The replacement of R=H by R=CH$_2$OH changes the chemical shift of H$_3$ by 0.3 ppm. Also we get significant changes of the charge densities at the triple bond atoms C$_1$ and C$_2$ but not at C$_3$ and H$_3$. In 6 the distances between H$_3$ and the triple bonds are a little smaller than in 7′. Therefore, it is not surprising that the error of our calculation is 0.37 ppm greater in 6 than in 7. If we correct the difference between the experimental shifts of H$_3$ of 6 and 7 by 0.37 ppm we obtain 2.52 ppm. Our calculation yields exactly the same difference between 6 and 7. It is nearly totally caused by the paramagnetic ring current in 7. Also the inner proton of the dehydro [18]-annulene 14 is

Table 2. Experimental and calculated ^{1}H-chemical shifts δ (in ppm) of 1–14

Compound	Proton	δ^{RC}	δ^{LA}	δ_1	δ_2	δ_{exp}	
1	1	-1.71	0.84	3.75	4.33	4.42-4.56[16,17,18]	
1′[a]	1	-5.48	1.21	-0.90	0.93		
2	1	-0.54	0.82	5.46	5.48	5.60[20]	
3	1,6	-1.64,-1.95	0.84,0.92	3.62[b]	4.29[b]	4.18[19]	4.27[18]
	2,5	-1.84,-1.84	1.08,1.17	3.55	4.49	5.03	5.16
	3,4	10.74,-2.17	0.83,1.22	12.55	10.51	10.90	11.18
	7,8	-1.80,-1.70	0.80,0.77	3.69	4.24	4.53	4.68
4	3,4	3.98,-0.35	1.30,1.56	8.92[b]	8.44[b]	8.78[20]	
	7,8	-0.54,-0.54	0.88,0.85	5.46	5.53	5.66	
5	3,4	2.65,0.02	1.47,1.60	8.22[b]	8.07[b]	8.60[20]	
6	3	3.88	1.45	11.95	10.39	13.13[13]	
	7	-0.38	-0.03	5.69	4.79	5.74/5.77	
	8	-0.39	0.97	5.69	5.78		
7[c]	3	1.31	1.51	7.97	7.87	10.24[d,13]	
8[c]	3	1.34	1.77	8.01	8.16	8.03[13]	
9	1	2.13	1.15	9.39	8.48	8.54[18]	-
	2	2.43	1.38	9.82	9.01	9.64	9.32[e,21]
	9	-10.67	1.21	-9.41	-4.26	-5.48	-4.44
10	1	2.07	1.17	9.30	8.45	-	-
	2	2.36	1.45	9.71	9.00	9.44[f,22]	9.52[g,23]
	3	2.55	1.69	9.99	9.43	9.74	-
	9	-9.94	1.31	-8.34	-3.43	-3.57	-3.47
	1′	1.75	1.50	8.62	8.30	8.58	8.81
11	3	1.95	1.57	9.57	9.12	8.88-9.12[h,24]	
	4	1.46	1.17	8.40	7.83	-	
	5	1.42	-0.55	8.35	6.08	-	
	6	1.63	1.51	8.65	8.35	8.22-8.44	
	7	1.61	1.30	8.62	8.12	8.26-8.41	
	8	1.46	1.01	8.40	7.68	-	
	9	-6.55	1.23	-3.36	-0.12	0.70-0.81	
	10	-6.81	1.03	-3.75	-0.58	0.60-0.71	
	1′	1.81	1.61	9.17	8.88	8.94-9.20	
	2′	1.24	1.46	7.88	7.75	7.74-7.83	
	3′	1.22	1.44	7.84	7.71	7.74-7.83	
	4′	1.62	1.48	8.44	8.16	8.52-8.59	
12	3	2.38	1.65	10.19	9.63	9.80[i,23]	
	4	1.86	1.22	8.98	8.28	-	
	6	2.26	1.82	9.57	9.28	-	
	7	2.06	1.41	9.27	8.67	9.17	
	8	1.86	1.13	8.98	8.18	-	
	9	-8.11	1.39	-5.65	-1.52	-1.22	
	10	-8.36	1.24	-6.01	-1.91	-1.53	
	1′	2.09	1.69	9.57	9.23	9.46	
	2′	1.57	1.59	8.35	8.23	8.37	
	3′	2.02	1.55	9.02	8.63	9.62	
	4′	1.62	1.43	8.43	8.10	8.64	

Table 2. (*Contd*)

Compound	Proton	δ^{RC}	δ^{LA}	δ_1	δ_2	δ_{exp}
13	3	2.84	1.65	10.12	10.09	10.22[j,22]
	4	2.32	1.18	10.43	8.70	-
	9	-9.98	1.45	-8.40	-3.33	-3.45
	1'	2.31	1.70	9.90	9.46	9.54
	2'	1.62	1.55	8.43	8.22	-
	3'	2.28	1.02	9.41	8.36	9.71
14	1	0.89	1.21	7.36	7.15	8.49[25]

[a]With standard bondlengths (cf. Table 1). [b]Average value for the indicated proton. [c]The geometry is chosen as in **6**. [d]Values of **7'**. [e]Values of **9'**. [f]Values of **10'**. [g]Values of **10''**. [h]Values of **11'**. [i]Values of **12'**. [j]Values of **13'**.

Table 3. ^{1}H-chemical shifts δ (in ppm) and net charge densities ΔQ calculated with the CNDO/2 method[12] of **7'**

R	δ_{exp}[a]	ΔQ_{C_1}	ΔQ_{C_2}	ΔQ_{C_3}	ΔQ_{H_3}
H	8.60	-0.041	-0.051	-0.025	-0.001
CH_2OH	8.90	-0.073	-0.030	-0.026	-0.001
CH_2Br	8.47				

[a]Ref.[13]

calculated 1.34 ppm at too high a field. It should be noted that δ^{RC} and δ^{LA} of this proton are smaller than the corresponding values of the α-proton of naphtalene ($\delta^{RC} = 1.12$, $\delta^{LA} = 1.47$ ppm). The difference between both δ^{RC} values has to be attributed to a small diamagnetic ring current in the 18-membered ring. The calculated shifts of the inner protons of the symmetrical [14] annulenes **9**, **10** and **13** agree approximately with the experimental values. Those of the unsymmetrical compounds **11** and **12** are obtained as expected 0.3–1.2 ppm at too high a field and the errors for the inner protons of the [12] annulenes **3**–**6** are 0.7–2.7 ppm. It follows that the additional downfield shift of the triple bond for the inner protons is greater if the triple bond length is shorter, although this effect was not encountered for the outer protons $H_{3'}$ or **12'** and **13'**. Obviously these different additional shifts cannot be accounted for by the McConnell equation.[11] This is in accord with the reasoning given in Ref. 6 against the applicability of the McConnell equation for distances <3 Å between the proton in question and the triple bond. In the case of **14** this equation would only give a shift of ~0.2 ppm to lower field[25] instead of ~1.3 ppm. In Ref. 25 it was possible to account for this downfield shift because the RC effect of the naphtalene units was greatly overestimated.

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