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CALCULATION OF ^{1}H-CHEMICAL SHIFTS OF KEKULENE AND SIMILAR COMPOUNDS[1]

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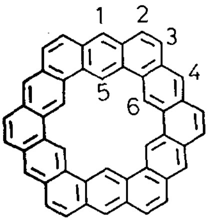
Diederich and Staab[2] have reported the synthesis of kekulene **1**. The ^{1}H-NMR spectrum of **1** clearly indicates that **1** cannot be considered as a system **1a** of weakly coupled annulenes since the inner protons of **1** are at lower field than the outer ones, cf. Table 1. This is in accordance with MO calculations[3] and calculations[4] of the ^{1}H-chemical shifts with a modified Hückel method (MHMO)[5] led to the same qualitative conclusions. The calculated shift for the inner proton H-5, however, is at too high a field even if the additional van der Waals deshielding[6] for hindered protons is taken into account. The MHMO method is a simplified version of the uncoupled Hartree-Fock perturbation theory[5] which has been shown[7] to be only a poor approximation to the exact coupled theory[8] when large conjugated hydrocarbons are concerned. Therefore, we have calculated the ^{1}H-chemical shifts δ of **1** - **3** within the coupled theory according to equation (1)[9] $\delta = \delta^{RC} + \delta^{LA} + \delta^{O}$, where δ^{RC} is the ring-current contribution of the π electrons to the chemical shift, δ^{LA} contains the local anisotropic effects of the π and σ electrons and δ^{O} includes all constant contributions to δ and ensures that $\delta_{TMS} = 0$.

The deshielding of the protons in benzene with respect to a noncyclic conjugated polyene is due to ring-current (δ^{RC}) and local anisotropic effects (δ^{LA})[9,10]. In benzenoid hydrocarbons which have only outer protons, i.e. protons at the periphery of the molecule, δ^{RC} is roughly proportional to δ^{LA}. In this case also equation (2) $\delta' = \delta^{RC} + \delta^{o}$ yields a good correlation between experimental and calculated shifts, whereas with annulenes only the combined consideration of δ^{RC} and δ^{LA} (equation (1)) can provide an explanation of the chemical shifts since δ^{LA} is positive (exceptions cf.[11]) and increases the deshielding of the outer protons of (4n+2) annulenes and decreases the shielding of the inner protons (δ^{RC} is positive for outer and negative for inner protons)[10,12].



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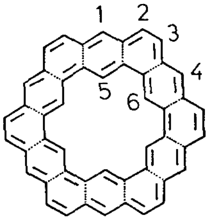
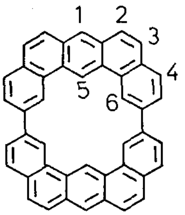


1a



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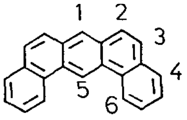

3

The calculated and experimental shifts of 1 - 3 are given in Table 1. The mean (maximal) deviation of the calculated values (equation (1) or (2)) from the experimental ones is only 0.1 (0.2) ppm. The implicit van der Waals corrections for hindered protons, e.g. H-6 in 3, in δ^{o} are only[9] 0.44 (δ') and 0.40 ppm (δ) and for doubly hindered protons, e.g. H-5 in 3, 0.81 and 0.75 ppm respectively. In contrast to the inner proton H-5, for which calculated and experimental δ are nearly identical, the calculated shifts of the outer protons of 1 are approximately 0.3 ppm at too low a field. Probably interaction with the solvent [D_3]-1,3,5-trichlorobenzene[2] leads to this highfield shift of the protons at the periphery of the molecule.

The deshielding of the outer and inner protons in 1 is due to δ^{RC} and δ^{LA}. Nevertheless δ and δ' are nearly the same for the outer protons, whereas for the inner protons of 1 the δ values are greater than the δ'

values due to the greater δ^{LA} of the inner protons with respect to the outer ones. In **1a** the δ^{LA} values are reduced by about 10% compared to those of **1**, whereas the δ^{RC} values of the outer protons of **1a** are greater by a factor of 4 than those of **1** and for the inner protons the factor amounts to 10. The δ^{RC} values are negative in **1a** and positive in **1**. This demonstrates that resonance structures like **1a** do not contribute significantly in **1**.

Table 1. Calculated[a)] and experimental ^{1}H-chemical shifts δ (in ppm) of **1** - **3**

Compound	Proton	δ^{RC} [b)]	δ^{LA}	δ'	δ	$\delta_{exptl.}$
1	1,4	3.33	1.80	8.78	8.71	8.37[2]
	2,3	2.68	1.67	8.25	8.22	7.94
	5,6	3.95	2.41	10.10	10.42	10.45
1a	1,4	13.88	1.65	17.41	14.44	
	2,3	11.75	1.59	15.67	13.19	
	5,6	-37.66	2.09	-23.92	-13.07	
2	1	3.01	1.76	8.52	8.50	
	2	2.39	1.68	8.01	8.07	
	3	2.25	1.68	7.90	7.99	
	4	2.31	1.71	7.95	8.06	
	5	4.23	2.37	10.33	10.54	
	6	4.32	1.71	9.59	9.93	
3	1	2.95	1.71	8.47	8.41	8.29[13]
	2	2.32	1.63	7.96	7.98	7.80
	3	2.18	1.60	7.84	7.87	7.66
	4	2.18	1.58	7.84	7.85	7.83
	5	3.80	2.05	9.98	9.98	9.98
	6	2.92	1.83	8.88	8.92	8.96

[a)] Bondlengths 0.1397 (C-C) and 0.108 nm (C-H). [b)] In order to obtain δ and δ' one has to multiply δ^{RC} by 0.5569 (δ) and 0.8176 (δ')[9].

The calculated δ and δ' values of the outer protons of **2** agree very well as they do in **1**. The δ values of the inner protons of **2** differ from the corresponding δ' values since the δ^{LA} contributions are greater for the inner than for the outer protons. This indicates that local anisotropic contributions to the ^{1}H-chemical shifts (equation (1)) have to be considered in condensed conjugated hydrocarbons with protons which are not at the periphery of the molecule.

REFERENCES

1) I am indebted to the Deutsche Forschungsgemeinschaft for financial support.

2) F. Diederich and H. A. Staab, Angew. Chem., 90, 383 (1978).

3) R. McWeeny, Proc. Phys. Soc., A64, 261, 921 (1951); G. Ege and H. Fischer, Tetrahedron, 23, 149 (1967); G. Ege and H. Vogler, Z. Naturforsch., 27b, 918 (1972).

4) G. Ege and H. Vogler, Theoret. Chim. Acta, 26, 55 (1972).

5) H. G. F. Roberts, Theoret. Chim. Acta, 15, 63 (1969).

6) Cf. C. W. Haigh, R. B. Mallion, and E. A. G. Armour, Mol. Phys., 18, 751 (1970) and references therein.

7) G. Ege and H. Vogler, Chem. Phys. Lett., 31, 516 (1975).

8) G. G. Hall and A. Hardisson, Proc. Roy. Soc. (London), A268, 328 (1962).

9) H. Vogler, J. Am. Chem. Soc., in press.

10) M. Barfield, D. M. Grant, and D. Ikenberry, J. Am. Chem. Soc., 97, 6956 (1975).

11) H. Vogler, Org. Magn. Res., in press.

12) H. Vogler, Tetrahedron, submitted.

13) C. W. Haigh and R. B. Mallion, Mol. Phys., 18, 737 (1970).

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