THEORETICAL STUDY OF GEOMETRIES AND 1H-CHEMICAL SHIFTS OF CYCLOARENES

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ABSTRACT

The geometries of the cycloarenes 1—6 with 9—12 annelated benzene rings are determined by means of a π-SCF force-field approach. 1H-chemical shifts are calculated by taking into account ring current and local anisotropic contributions. The importance of annulenoid resonance structures is discussed.

INTRODUCTION

Cycloarenes consist of cyclic cata-condensed or annelated [1] benzene rings so that the arene units form a macrocyclic conjugated system where the internal cavity contains C—H bonds [2]. Compounds 1—6 in Fig. 1 constitute cycloarenes with 9—12 benzene ring units. Topologically, cycloarenes are characterized by a monocyclic characteristic graph [3]. Such a definition excludes compounds like coronene or some of the so-called corannulenes or circulenes [4, 5].

The only cycloarene hitherto known is kekulene 6 [2]. Attempts to synthesise the other cycloarenes are under way [6]. Kekulene possesses 200 Kekulé resonance structures [7], e.g., structures A and B in Fig. 2. A constitutes one of the possible four Kekulé structures for two concentric [4m + 2] perimeters thus forming a "super sextet" [8]. B together with other corresponding Kekulé structures gives rise to Clar's notation [9] with "aromatic sextets" and quasi localized double bonds, see Fig. 1. A super sextet can also be formulated for 1, 2, 4, and 5, however, with [4m] perimeters in case of 1 and 4. Usually cata-condensed benzenoid hydrocarbons belong to the class of alternant hydrocarbons which are characterized by a uniform charge distribution [1]. This does not apply to the non-alternant hydrocarbon 3 since it cannot be embedded in a regular hexagonal two-dimensional lattice. Furthermore, a super sextet is impossible for 3 since at least one radial double bond has to be written due to the odd number of carbon atoms in inner and outer perimeter.
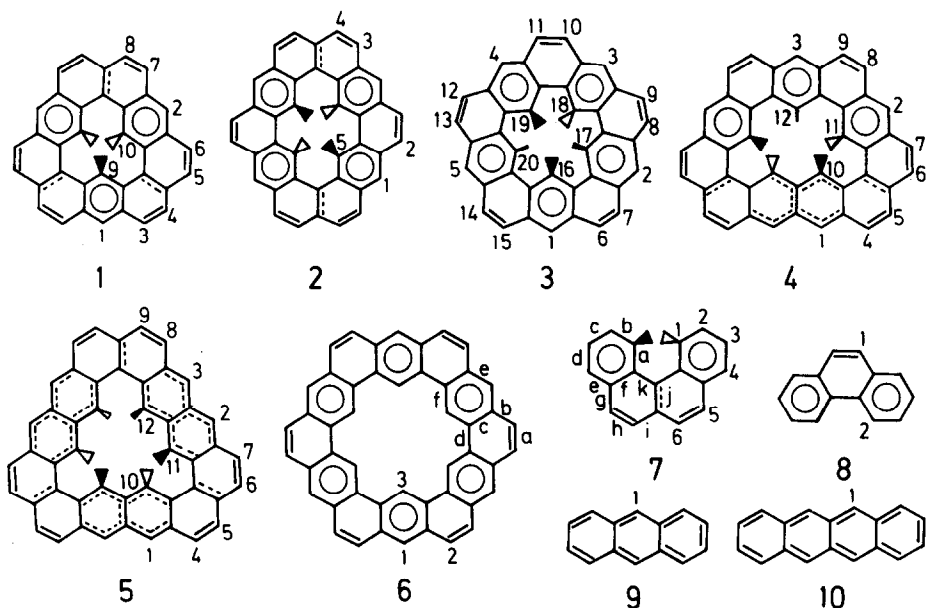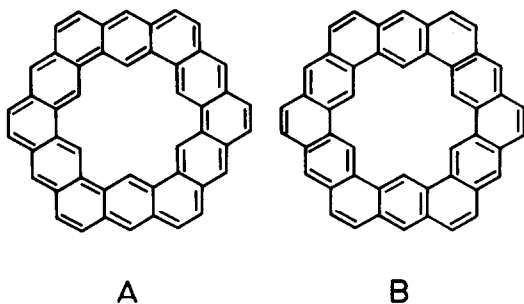
Fig. 1. Survey of compounds under study.

Fig. 2. Two Kekulé structures for kekulene 6.

Earlier theoretical investigations of 1, 2, 4—6 [10—12] demonstrated that Kekulé structures of type A should not be dominant in the description of the electronic properties of these cycloarenes. This was corroborated in case of 6 by the experimental determination of the molecular structure [13], other physical properties [11], and especially ^{1}H-chemical shifts [2] which represent a sensitive probe for the electronic structure of conjugated compounds. The hollow space formed by the inner perimeter in case of the as yet unknown cycloarenes 1—5 is too small in order to allow a planar carbon skeleton. This was not taken into consideration in the earlier theoretical investigations [10—12]. Therefore, we wish to report in this communication our studies on molecular geometries and ^{1}H-chemical shifts of cycloarenes

1—6. Semiempirical methods had to be applied since ab initio procedures are hardly feasible with such extended systems.

COMPUTATIONAL PROCEDURES

The geometries of all compounds studied in this paper have been determined by means of the π-SCF force-field method of Lindner [14] which was already successfully applied to strained benzenoid hydrocarbons [15].

The ^{1}H-chemical shifts are calculated with the procedure of ref. 16 which reproduces the experimental shifts of 6 sufficiently [17]. The proton shift δ is obtained as a sum $\delta = \delta^{RC} + \delta^{LA} + \delta^{q} + \delta^{o}$ where δ^{RC} constitutes the ring current contribution of the π-system and δ^{LA} the local anisotropic contributions of π- and σ-electrons. δ^{q} is a shift due to a net charge Δq at the carbon atom of the C—H bond. δ^{o} contains all contributions to δ which do not depend on the topology of the molecule and it defines the zero of the δ-scale.

With benzenoid hydrocarbons the simpler formula $\delta' = \delta^{RC} + \delta^{o}$ leads to equally good results [16], however, this is not true for annulenoid systems where a quantitative satisfying assessment of ^{1}H-chemical shifts requires the inclusion of δ^{LA} [18]. The formulae for δ^{LA} assume planar compounds [16]. Therefore, in case of the non-planar cycloarenes 1—5 we calculated δ^{LA} for a corresponding planar model with ideal geometry, i.e., all bond lengths are fixed at 140 pm and regular polygons are used. Nevertheless we expect that our δ^{LA} values are in the correct order of magnitude especially if the local deformations around a carbon atom in the conjugated system are small.

For overcrowded protons δ^{o} includes a so-called van der Waals shift to lower field [19]. In case of 3 and 6 we used the values of ref. 17 whereas the van der Waals shift for the inner protons of 1, 2, 4, and 5 have been determined as 1.10 (δ') and 0.37 ppm (δ) by comparing calculated and experimental shifts for H_1 of 7. The value for δ' is similar to that derived within a Hückel approach [20].

RESULTS AND DISCUSSION

Molecular geometries

Kekulene 6 is essentially a planar molecule [13]. The calculated bond lengths agree well with the experimental ones; the absolute mean error is only 1 pm, see Table 1. The carbon skeleton of [4]helicene 7 appears as a subunit in cycloarenes 1—5. According to X-ray analysis [21] 7 is not planar and possesses approximate C_2 symmetry. The calculated bond lengths agree with the experimental ones as well as in case of 6, see Table 1. Also the experimental deviations of the atoms from the mean molecular plane are well reproduced by the π-SCF force-field procedure, see Fig. 3. Therefore we expect that reliable structures are also obtained for the non-planar cyclo-arenes 1—5.

TABLE 1

Calculated (r) and experimental (r_{exp}) bond lengths (in pm) of kekulene **6** and [4]helicene **7**

Compound	Bond[a]	r	r_{exp}	Reference
6	a	136.1	134.7	[13]
	b	145.4	144.5	
	c	142.3	142.5	
	d	147.7	145.9	
	e	140.6	139.8	
	f	140.0	138.8	
7	a	142.0	143.3[b]	[21]
	b	138.0	137.8	
	c	141.2	140.9	
	d	137.9	137.4	
	e	141.9	139.1	
	f	142.0	143.1	
	g	143.7	144.3	
	h	136.3	134.2	
	i	143.6	143.0	
	j	140.7	141.2	
	k	146.6	144.6	

[a]See Fig. 1. [b] Averaged values.
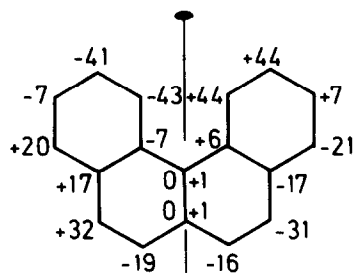
Calculated/Experimental

Fig. 3. Calculated (left half) and averaged experimental [21] (right half) deviations of carbon atoms of [4]helicene **7** from the mean molecular plane.

The C—C bonds in **1—8** can be divided into three classes: (i) very short bonds with lengths r = 135.9—137.5 pm which we can consider as quasi localized double bonds, (ii) bonds with r = 137.9—143.3 pm which we will call "aromatic" bonds, and (iii) long bonds with r = 143.4—148.1 pm which correspond to quasi single bonds. We obtain the formulae of Fig. 1 if we distinguish these bond classes simply by (i)═, (ii) ╍╍, and (iii) ——. Furthermore we used Clar's sextet notation [9] if all bonds in a 6-ring are aromatic. The carbon skeletons of **7** and **8** form subunits of **1—6**. Indeed the bond lengths

pattern of **7** appears in **1** and **2** and that of **8** in **2—4** and **6**. The cycloarenes **3** and **6** can be considered as built up from repeated phenanthrene units **8**. Other substructures besides **7** and **8** occur in **4** and especially in **5**. According to the geometric structures none of the cycloarenes **1 –6** can exhibit considerable annulenoid character the more the inner and outer perimeter contain quasi single bonds.

The deviations of inner hydrogens and carbon atoms of **1—5** from the mean molecular plane are shown schematically in Figs. 1 and 4. The inner protons of **2** are alternately up and down. This is not true with the other non-planar cycloarenes which is in case of **1, 3,** and **4** already due to the odd number of inner hydrogens. The 6-ring units of **3** which carry the inner protons are characterized by a benzene sextet. These 6-rings form the carbon skeleton of penta-*m*-phenylene whose experimental deviation pattern of the inner protons [22] corresponds to the calculated one of **3**. The deformations in the macrocyclic compounds **1—5** lead to reasonable distances between the inner protons of $\geqslant 174$ pm (**1**) and $\geqslant 190$ pm (**2—5**). The latter value corresponds approximately to that between the overcrowded protons H_2 in phenanthrene **8**. Assuming planar conformations one would have $H \cdots H$ separations of less than 100 pm. In case of the smallest studied cycloarene **1** inner and outer perimeter deviate to the same extent from the mean molecular plane whereas with **2** the outer and with **3—5** the inner perimeter deviates more than the other one. Finally, it should be mentioned that the

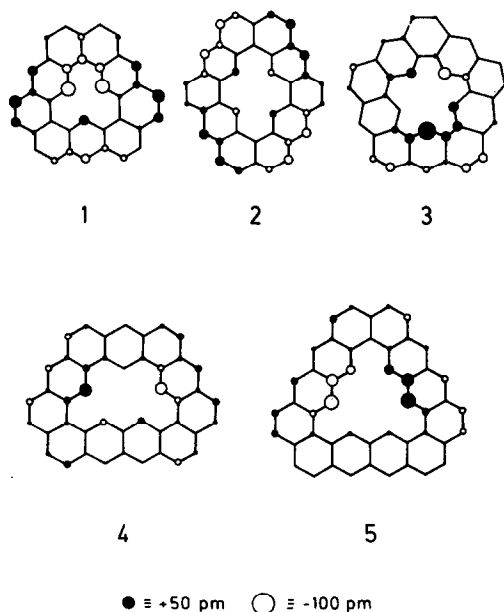$\bullet \equiv +50$ pm $\bigcirc \equiv -100$ pm

Fig. 4. Schematical representation of the calculated deviations of carbon atoms of cycloarenes 1– 5 from the mean molecular planes.

distortions along the C—C bonds are small so that the application of a π-electronic approach is still justified.

^{1}H-chemical shifts

The calculated (δ and δ') and experimental (δ_{exp}) ^{1}H-chemical shifts of 6 and 7 are given in Table 2. The differences between δ' and δ are insignificant and both reproduce the experimental values with an absolute mean error of less than 0.1 ppm. The maximum errors are less than 0.3 ppm. The calculated shifts δ and δ' of the cycloarenes 1—6 are given in Table 3. A dominant annulenoid character resulting from negligible coupling between the concentric perimeters would lead to shifts of outer (δ_o) and inner (δ_i) protons which are characterized by $\delta_i \gg \delta_o$ in case of 1 and 4 with [$4m$] perimeters respectively $\delta_o \gg \delta_i$ for 2, 5, and 6 with [$4m + 2$] perimeters. The mean value of δ_i and δ_o should be around 5—6 ppm. However, as Table 3 reveals, all shifts appear at low field, i.e., inner and outer protons experience a diamagnetic ring current effect irrespective of the type of perimeter. Thus we can conclude from the calculated shifts that all the studied cycloarenes do not show an appreciable annulenoid character. This also rationalizes the good agreement between δ and δ' and we need only to discuss the δ values.

The protons in 1—6 are either located at linearly annelated benzene rings (type A) which are all characterized by aromatic bonds or even sextets, or they are located at angularly annelated 6-rings (type B). Inner protons belong all to type A with 1—6. They are at lowest field in the NMR spectrum due to their close proximity to several other benzene rings. All outer protons of type B are located at a quasi localized double bond. Consequently they are at higher field than the outer A type protons. In 1 and 4 with [$4m$] and 3 with [$4m + 3$] perimeters the type A protons exhibit similar chemical shifts (8.18—8.47 ppm) like H_1 of anthracene 9 (8.22 ppm) whereas in 2, 5,

TABLE 2

Calculated (δ' and δ) and experimental (δ_{exp}) ^{1}H-chemical shifts of kekulene 6 and [4] helicene 7 (values in ppm)

Compound	Proton[a]	δ'	δ	δ_{exp}	Reference
6	1	8.53	8.57	8.37	[2]
	2	7.95	8.01	7.94	
	3	10.16	10.45	10.45	
7	1	9.10	9.10	9.10	[24]
	2	7.53	7.62	7.62	
	3	7.45	7.51	7.52	
	4	7.81	7.81	7.95	
	5	7.78	7.83	7.82	
	6	7.81	7.88	7.75	

[a] See Fig. 1.

TABLE 3

Calculated ^{1}H-chemical shifts δ' and δ (in ppm) of the cycloarenes 1—6

Compound	Proton[a,b]	δ'	δ	Proton[a,c]	δ'	δ	Proton[a,d]	δ'	δ
1	1	8.28	8.39	3	7.76	7.91	9	11.18	11.17
	2	8.20	8.34	4, 5, 8	7.66	7.85	10	11.31	11.26
				6	7.69	7.86			
				7	7.73	7.89			
2	1	8.60	8.62	2	7.88	8.00	5	9.55	9.76
				3	8.17	8.20			
				4	8.12	8.16			
3	1	8.14	8.26	6	7.73	7.94	16	9.60	10.28
	2	8.20	8.24	7	7.74	7.94	17	10.22	10.70
	3	8.15	8.27	8, 10	7.68	7.90	18	9.33	10.10
	4	8.18	8.28	9	7.69	7.91	19	9.86	10.46
	5	8.21	8.30	11, 14	7.67	7.90	20	9.98	10.54
				12	7.75	7.95			
				13	7.76	7.96			
				15	7.66	7.89			
4	1	8.47	8.47	3	7.81	7.95	10	11.23	11.13
	2	8.31	8.38	4	7.73	7.91	11	10.86	10.91
	3	8.20	8.18	5	7.82	7.91	12	10.37	10.93
				6	7.91	8.02			
				7	7.67	7.86			
				8	7.66	7.82			
5	1—3	8.73	8.65	4, 7, 8	8.01	8.09	10	9.93	10.16
				5, 6	7.88	8.01	11	10.05	10.24
				9	7.90	8.02	12	10.13	10.29
6	1	8.53	8.57	2	7.95	8.01	3	10.16	10.45

[a]See Fig. 1. [b]Outer A-type proton. [c]Outer B-type proton. [d]Inner A-type proton.

and 6, with [4m + 2] perimeters they are at even lower field (8.57—8.65 ppm) than H$_1$ of tetracene 10 (8.41 ppm). Analogously, the type B protons of 2, 5, and 6 are at significantly lower field (8.00—8.20 ppm) than those of 1, 3, and 4 (7.82—8.02 ppm) with values more similar to that for H$_1$ of phenanthrene 8 (7.79 ppm). On the other hand the inner protons of the [4m] perimeter cycloarenes 1 and 4 are at lower field (10.91—11.26 ppm) than those of the [4m + 2] perimeter compounds 2, 5, and 6 (9.76—10.45 ppm) whereas they hold an intermediate position in case of 3 (10.10—10.70 ppm). This (de)shielding of the (outer) inner protons of cycloarenes with [4m + 2] perimeters by 0.2—0.6 ppm with respect to those with [4m] or [4m + 3] perimeters indicates a small influence of the annulenoid Kekulé structures A (see Fig. 2) on ^{1}H-chemical shifts.

The different outer protons belonging to the same type in a cycloarene differ less than 0.3 ppm in their chemical shifts. Larger variations are found for inner protons due to the greater differences in their geometrical orientation to other parts of the inner perimeter. The chemical shifts of protons of

the same type in the isomeric cycloarene pairs **2/3** and **5/6** are significantly different only if the perimeters have different sizes as in **5/6**.

The alternant hydrocarbons **1, 2, 4—6** have uniform charge distribution so that all $\Delta q = 0$ and hence δ^q vanishes for all protons. On the contrary the non-alternant hydrocarbon **3** exhibits net charges Δq, however, they are small ($|\Delta q| < 0.02$). Since $\delta^q \cong 10\Delta q$ [23] the resulting shifts due to the non-uniform charge distribution are small as well ($|\delta^q| < 0.2$ ppm).

CONCLUSION

The geometries of the non-planar cycloarenes **1—5** were determined by means of the π-SCF force-field method of Lindner [14] which yields for the planar kekulene **6** and the helical **7** geometries which are in good agreement with the experimental ones. Inner and outer perimeters of **1—5** are deformed in such a way that the energetically unfavourable non-bonded interactions between the inner protons are sufficiently reduced. Both the geometries as well as the ^{1}H-chemical shifts of **1—6** demonstrate that the electronic structure is not dominated by annulenoid conjugation which manifests itself only in a small down (high) field shift of the outer (inner) protons of cycloarenes with [$4m + 2$] perimeters with respect to those with [$4m$] or [$4m + 3$] perimeters.

Could we expect a more pronounced annulenoid character in other cycloarenes? This might be the case if one could find a cycloarene where none of all possible Kekulé structures contains a radial double bond. Such systems would contain two disjoint annulene resonance structures and are called "conjugation deficient" compounds [5]. However, conjugation deficient cycloarenes cannot be formulated since, for one thing the concentric perimeters need to have each an even number of carbon atoms in order to write down resonance formulae like A in Fig. 2, and for another there must be angular annelated benzene rings and it is always possible to write at least for one of them two radial double bonds. Conjugation deficient compounds are only obtained if benzene rings are conveniently replaced by odd membered rings.

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