Maximum Overlap Study of Some Bridged Annulenes

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The electronic and geometrical structures of 9,10-methano[10]annulene, 11,11-dimethyl-9,10 methano[10]annulene and 9,10-ethano-9,10 dihydronaphthalene are studied by the maximum overlap method. It is found that the first two molecules have bisnorcaradiene structures possessing very weak central bonds described by sp^7 hybridisation states. Bending of these hybrid orbitals is highly pronounced indicating that the most probable place for electrophilic attack is the central bond on the side opposite from the bridge. Their overlapping is, however, by no means negligible concomitant with the experimental NMR evidence which suggests the presence of a direct bond between the bridgehead atoms. The calculated bond angles are in good accordance with available experimental data. The present results provide rationalization of the unusual dihedral angle of 136° found in 9,10-methano[10]annulene by X-ray measurements. Thus the current opinion that bridged annulenes tend to achieve a planar configuration of the olefinic carbon atoms in order to maximize conjugation between the rings should be revised.

Introduction

The local hybrid orbitals proved very useful in discussing many physical and chemical properties of hydrocarbons since the hybridisation ratio has a profound effect on C-C, C-H and Si-C spin-spin coupling constants [1], thermodynamic acidity [2] and C-H stretching frequencies [3]. It affects also the proton isotropic hyperfine constants in planar radicals [4], nuclear quadrupole coupling constants [5], etc. The extent of overlapping of the neighbouring hybrids forming covalent bonds is linearly related to: C-C and C-H bond energies [6], heats of formation and atomisation of molecules and strain energies [7, 8]. Hybridisation is apparently the most important local bond parameter. It is therefore of some interest to evaluate hybridisation ratios for molecular systems exhibiting unusual structural features. In this paper we report on maximum overlap approximation (MOA) calculations performed on 9,10-methano[10]annulene, 11,11-dimethyl-9,10-methano[10]annulene and 9,10-ethano-9,10-dihydronaphthalene. The calculations for the first two molecules of this series of bridged annulenes were executed by using the experimentally determined bond lengths. The geometry of 9,10-ethano-9,10-dihydronaphthalene is not known, and it is predicted by the iterative maximum overlap approximation (IMOA) method [9]. The electronic structure of the molecules mentioned above is then discussed in terms of the evaluated hybrid orbitals.

Outline of the Calculations

The details of the MOA method have been described elsewhere [1–4], and only the main features are given here. The MOA approach is based on the idea that atoms are distorted in a molecule. The distorted atomic orbitals called hybrids are of the form

$$\psi_{Aj} = a_{Aj}(2s)_A + (1 - a_{Aj}^2)^{1/2}(2p)_{Aj}, \qquad (1)$$

where A denotes the carbon nucleus in question and the index $j\,(j = 1-4)$ specifies the particular orbital placed on that nucleus. The variable parameter a_{Aj} measures the relative contribution of 2s and 2p orbitals in the hybrid. The hybrids placed on the same atom are constrained to be orthogonal. This requirement is introduced on the basis of the intuitive argument that orbitals with the same spin should avoid each other as much as possible. The easiest way of seeing this is to go over to the limiting case in which the nonorthogonal spatial wave functions are identical [10]. In this case the spins would be antiparallel and their valencies would be internally saturated. This point of view was justified by numerous semiempirical calculations [11]. It turned out that the local hybrid orbitals extracted

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from CNDO/2 and SCC (self consistent charge) MO wave functions overlap by amounts smaller than 0.1. The orthogonality conditions provide a set of relationships of the form

$$a_{Ai}\, a_{Aj} + (1 - a_{Ai}^2)^{1/2} (1 - a_{Aj}^2)^{1/2} \cos \vartheta_{ij} = 0 \,, \qquad (2)$$

where ϑ_{ij} represents the angle between the axes of the hybrids ψ_{Ai} and ψ_{Aj}. The hybridisation parameters a_{Ai} are determined by the maximum overlap criterion i. e. one searches for the maximum of the sum of all bond overlap integrals in molecules

$$E = k_{CC} \sum_{C-C} S_{CC} + k_{CH} \sum_{C-H} S_{CH} \,, \qquad (3)$$

where $S_{AB} = \int \psi_A \psi_B \, dv$ is the overlap integral and k_{CC} and k_{CH} are the proportionality constants between the bond energy and bond overlaps. We used Clementi "double zeta" atomic wave functions [12] and the bond energy weighting factors k_{CC} and k_{CH} of 121.2 and 135.9 kcal/mole, respectively. These values reproduce the experimental bond energies in methane and ethane. Consequently the requirement of the maximum overlapping (cf. (3)) is in fact equivalent to the requirement of the maximum of the sum of all bond energies in a molecule. During the calculations it was assumed that the hybrid orbitals perfectly follow the C-H bonds as well as C-C bonds belonging to acyclic parts of a molecule. However, in cyclic molecules the so called bent bonds necessarily appear [13 – 15] and the hybrids do deviate from the straight line passing through the neighbouring nuclei.

The iterative maximum overlap method was discussed in detail earlier [9]. Briefly, we found that there are very good linear relationships between S_{CC} and S_{CH} bond overlaps and the corresponding CC and CH bond distances. These empirically established relations enable the prediction of interatomic distances * in an iterative fashion and this provides a basis for the IMAO method. One starts the calculation by assuming certain C-C and C-H bond distances and carries out the usual maximum overlap procedure. The resulting S_{CC} and S_{CH} overlap integrals are substituted into empirical correlations and the new set of bond distances is deduced. The whole cycle is repeated and the procedure continued until self consistency between the input and output bond lengths is achieved. Usually four or five iterations will suffice to obtain consistency. In order to reduce the large number of parameters it was assumed that atoms forming six-membered rings are coplanar for molecules considered in this paper.

Results and Discussion

The molecules considered here and the numbering of atoms are shown in Figure 1. 9,10-methano-[10]annulene and 11,11-dimethyl-9,10-methano-[10]annulene are very interesting 10π electron systems. Their skeletons bear formal analogy to naphthalene with the exception that the bond in common of the two six-membered rings is replaced by a non-conjugating bridge: either a methylene or dimethyl-substituted methylene group. These molecules can be considered as [10]annulenes on the basis of NMR experiments which established the delocalized nature of 10π-electrons [18]. It was argued that the X-ray crystal structure of 11,11-dimethyl-9,10-methano[10]annulene is not concomitant with the idea of π-electron conjugation [19]. However, we would like to point out that the C-C bond lengths are very insensitive to π-electron bond orders and that they are, in fact determined mainly by the states of the bondig hybrids [20] and their overlap

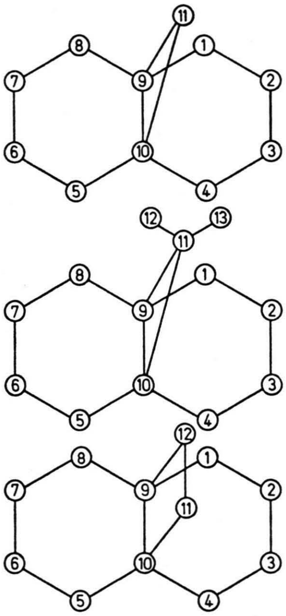

Fig. 1. Schematic representation of 1,6-methano[10]annulene, 11,11-dimethyl-1,6-methano[10]annulene and 9,10-ethano-9,10-dihydronaphthalene.

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* In strained systems one has to distinguish between the bond lengths and bond distances. For a thorough discussion one should consult refs. [16, 17].

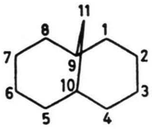
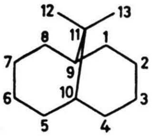
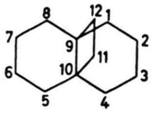
integrals [21], the π-electron correction being a perturbation of the σ-skeleton. The π-bond orders are responsible for the variation of C-C bond lengths only in planar molecules possessing the same state of hybridisation e. g. benzenoid hydrocarbons [22]. Therefore, the bisnorcaradiene structure of 11,11-dimethyl-9,10-methano[10]annulene revealed by X-ray measurements does not necessarily imply that the double bonds can be considered as perfectly localised. Some delocalisation may take a part without significant influence on the bond distances. In fact, the calculated proton chemical shifts indicate the presence of appreciable ring currents (vide infra).

The calculated hybrid orbitals and overlap integrals are presented in Table 1. The most striking feature of the results is that the hybrids are of the noninteger form although in many cases they are close to the canonical sp^2 and sp^3 cases. The hybrids describing the C_9-C_{10} bond have very little s-content being practically almost pure p-orbitals. The corresponding overlap integral is relatively small (0.46) but appreciable. Since it is not negligible, we conclude that in 9,10-methano[10]annulene and 11,11-dimethyl-9,10-methano[10]annulene we have a very weak and long (1.8 Å [19]) C_9-C_{10} bond. This is in accordance with NMR evidence which suggested the presence of a direct bond between the C_9 and C_{10} carbon atoms [25]. The hybrid orbitals are very similar for 9,10-methano[10]annulene and 11,11-dimethyl-9,10-methano[10]annulene illustrating the well known fact that the hybrids describing similar structural groups are transferable to a high degree. The C_{11}-H hybrid is of the sp$^{2.66}$ form being very close to the sp$^{2.62}$ composition found in cyclobutane. A very sensitive probe of the hybrid's s-character is provided by the spin-spin coupling constants of the directly bonded nuclei. By using the semiempirical relationship [1]:

$$J(\text{C-H}) = 1079\, a_{\text{CH}}^2/(1 + S_{\text{CH}}^2) - 54.9\ \text{Hz} \qquad (4)$$

we calculated that the C_{11}-H coupling constant in 9,10-methano[10]annulene is 138.1 what is in fair agreement with the experimental value of 142 Hz. The deviation angles of the hybrid orbitals from the straight lines passing through the neighbouring atoms provide a qualitative measure of the angular strain. One observes (Table 1) that the bridge is the most strained part in these molecules. The largest deviations are found in the weak C_9-C_{10} bond indicating that this bond is the most probable position

Table 1. The calculated hybridisation ratios, overlap integrals and deviation angles for 9,10-methano[10]annulene, 11,11-dimethyl-9,10-methano[10]annulene and 9,10-ethano-9,10-dihydronaphthalene.

Molecule	Bond	Hybridisation ratios[a] n-m	Overlap integrals	Deviation angles
	C_1-C_2	1.72–1.72	0.764	$d_{91} = 1.8°$
	C_2-C_3	2.02–2.02	0.726	$d_{12} = 0.3°$
	C_4-C_{10}	2.14–2.15	0.7118	$d_{23} = -2.7°$
	$C_{10}-C_{11}$	3.17–3.4	0.631	$d_{10\,11} = 22.7°$
	C_9-C_{10}	6.95–6.95	0.4611	$d_{9\ 10} = 26.8°$
	C_1-H	2.15	0.741	
	C_2-H	2.39	0.738	$d_{11\,10} = 16.7°$
	$C_{11}-H$	2.66	0.724	
	C_1-C_2	1.73–1.73	0.763	$d_{91} = 1.5°$
	C_2-C_3	2.03–2.03	0.726	$d_{12} = 0.1°$
	C_4-C_{10}	2.13–2.16	0.712	$d_{23} = -1.5°$
	$C_{10}-C_{11}$	3.07–3.33	0.633	$d_{10\,11} = 22.7°$
	$C_{11}-C_{12}$	2.72–3.20	0.661	
	C_9-C_{10}	7.21–7.21	0.460	$d_{9\ 10} = 26.1°$
	C_1-H	2.18	0.741	$d_{11\,10} = 17.2°$
	C_2-H	2.29	0.739	
	$C_{12}-H$	2.94		
	C_1-C_2	1.63–1.65	0.773	$d_{91} = -1.5°$
	C_2-C_3	2.24–2.24	0.702	$d_{12} = 0.9°$
	C_4-C_{10}	2.22–2.71	0.688	$d_{21} = 0.1°$
	C_9-C_{10}	3.18–3.18	0.6429	$d_{23} = 0.1°$
	$C_{10}-C_{11}$	3.49–3.72	0.625	$d_{10\,11} = 7.7°$
	$C_{11}-C_{12}$	3.30–3.30	0.604	$d_{11\,10} = 8.3°$
	C_1-H	2.21	0.741	$d_{9\ 10} = 9.6°$
	C_2-H	2.17	0.743	
	$C_{11}-H$	2.59	0.730	

[a] The hybridisation ratio n is defined as $n = a^2/(1 - a^2)$ where a is a coefficient of the 2s orbital.

of electrophilic attack. Needless to say, the corresponding hybrids are bent in the direction opposite from the bridge. The quantitative assessments of the strain energies can be obtained by using the available semiempirical correlations [7, 8].

The orthogonality conditions (2) enable the theoretical prediction of the molecular angles. The calculated angles for 11,11-dimethyl-9,10-methano-[10]annulene are in reasonable agreement with experimental data (Table 1). In spite of the relatively large deviation of the predicted dihedral angle from the measured value (7.5°), the present results do provide some rationalization of its unusual value of 136°. Thus the dihedral angle is determined mostly by the hybridisation of the bridgehead carbon atoms. This finding is not compatible with the current opinion that bridged annulenes tend to achieve the planar configuration of the olefinic carbons in order to ensure the most effective overlapping of π-orbitals, or in other words, the largest π-conjugation. Therefore, we conclude that conjugation between two benzene moieties is substantially smaller than that in naphthalene.

The chemical shift is a sensitive measure of the electron charge redistribution accompanying the formation of chemical bonds. According to Pople [23], the magnetic shielding of a nucleus A can be written as

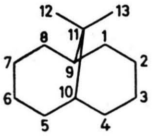
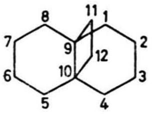
$$\sigma_A = \sigma_d + \sigma_p + \sum_{B \neq A} \sigma_{AB}\,, \tag{5}$$

where σ_d is the diamagnetic term, σ_p the paramagnetic term and σ_{AB} represents the effect of circulation of electrons localized on other atoms denoted by B. If the conjugated systems are considered then an additional term σ' arises in the expression (5) originating in the circulation of π-electrons. It is called the ring current term. The paramagnetic term σ_p includes mixing of the excited states and may be neglected for hydrogens because the excited states of this atom lie relatively high. However, the remaining three contributions σ_d, σ_{AB} and σ' are usually comparable in magnitude when shielding of protons is calculated. Randić and Majerski [24] tried to relate proton chemical shifts to hybridisation of the carbon atom in question and obtained the following correlation

$$\tau = 5(n-1)\,. \tag{6}$$

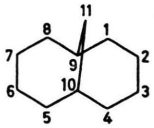
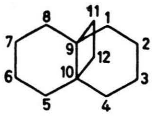
Employing the formula (6), the proton chemical shifts in 9,10-methano[10]annulene and 9,10-ethano-9,10-dihydronaphthalene are evaluated and the results are displayed in Table 3. The estimated chemical shifts are qualitatively well reproduced but the quantitative agreement with measured values is poor. One reason for this failure is the neglect of the ring current effect in 9,10-methano[10]annulene. However, if we take into acoount the ring current corrections as estimated by Haddon [25] (Table 3), the deviations from the experimental data are smaller but they are still considerable. The linear relation between chemical shifts and p-character of the ψ_{CH} hybrid orbitals is apparently too simple to encompass a large variety of magnetic environments of protons in molecules. This is not surprising

Table 2. Comparison between the calculated and experimental bond angles for 11,11-dimethyl-9,10-methano[10]annulene and the theoretically predicted geometry of 9,10-ethano-9,10-dihydronaphthalene.

Molecule	Bond distances	Bond angles	
		calculated	experimental
		$C_9-C_{10}-C_4 = 113.7°$	
		$C_9-C_1-C_2 = 121°$	124°
		$C_1-C_2-C_3 = 125.2°$	123°
		$C_{12}-C_{11}-C_{13} = 111.6$	109°
		$\alpha^a = 143.4°$	136°
	$d(C_1-C_2) = 1.320$	$C_9-C_{10}-C_4 = 115.7°$	
	$d(C_1-C_9) = 1.495$	$C_9-C_1-C_2 = 123.3°$	
	$d(C_9-C_{10}) = 1.542$	$C_9-C_{10}-C_{11} = 90.1°$	
	$d(C_2-C_3) = 1.478$	$C_{10}-C_{11}-C_{12} = 89.9°$	
	$d(C_{10}-C_{11}) = 1.565$	$\alpha^a = 130.2°$	
	$d(C_{11}-C_{12}) = 1.548$		
	$d(C_1-H) = 1.081$		
	$d(C_2-H) = 1.080$		
	$d(C_{11}-H) = 1.092$		

[a] α is a dihedral angle between the planes of six-membered rings.

Table 3. Comparison between the calculated and experimental proton chemical shifts for 9,10-methano[10]annulene and 9,10-ethano-9,10-dihydronaphthalene.

Molecule	Chemical shifts		Ring current[b] correction
	calculated	experimental[a]	
	$\tau_1 = 5.75$	2.896	− 1.144
	$\tau_2 = 6.95$	3.182	− 0.820
	$\tau_{11} = 8.35$	10.486	2.759
	$\tau_1 = 6.05$	4.50	
	$\tau_2 = 5.85$	4.50	
	$\tau_{11} = 7.97$	7.45	

[a] Experimental data were taken from the review article: R. C. Haddon, V. R. Haddon, and L. M. Jackman, Topics in Current Chemistry **16**, 103 (1971).

[b] Corrections due to ring currents were estimated by R. C. Haddon, Ref. [25].

because the underlying assumption of the relationship (6) is that terms σ_{AB} and σ_p are negligible, not to mention the ring current contribution. However, even if the diamagnetic term σ_d is retained only, a more careful analysis reveals that chemical shift τ_H is a complicated function of hybridisation parameter, overlap integrals and $1/r_{CH}$, where r_{CH} is the C-H internuclear distance. Therefore, some more theoretical work is needed here.

To conclude, the interesting [10]annulenes 9,10-methano[10]annulene and 11,11-dimethyl-9,10-methano[10]annulene have bisnorcaradiene structure with a relatively weak central bond formed by sp^7 hybrid orbitals. They are highly bent (26°) toward the space region between the wings of the molecules. In view of the high p-content and large bending deviation angles we conclude that the central bond is appreciably more strained than that in cyclopropane. The relatively small dihedral angles between the six-membered units of these molecules are dictated by the hybridisation states of the bridgehead carbon atoms. A certain amount of π-electron delocalization seems to be present affecting chemical shifts of the protons bound to sp^2 carbon atoms.

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