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Note

Hybridization in 1,5,9-Tridehydro(12)Annulene

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The hybridization in 1,5,9-tridehydro(12)annulene has been calculated by the method of maximum overlap. The results show that the hybrids describing CC double bonds and CC triple bonds have more *s*-character than the hybrids of the same carbon atoms involved in single CC bonds. Consequently, CC double and CC triple bonds are strengthened not only by the additional π-type overlap, but also by an increase of σ-type overlap, which accompanies the rise of the *s*-content. By using available empirical correlations a comparison between calculated and experimental NMR data (spin-spin coupling constant J (C^{13}—H) and chemical shift τ) is made.

In the present note we investigate the hybridization in 1,5,9-tridehydro (12)annulene, a large macrocyclic system containing CC double and triple bonds (Fig. 1.). The method of maximum overlap has been described in detail in earlier calculations of hybridization in cyclic and polycyclic hydrobarbons (see for example ref. 1 and references therein).

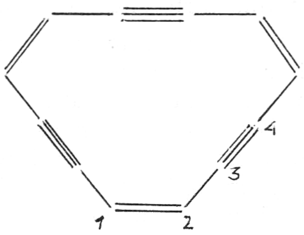

Fig. 1. Schematic diagram and numbering of atoms in 1,5,9-tridehydro(12)annulene.

Bond lengths assumed in the calculations are those suggested by Dewar and Schmeising[2]. The basic overlap integrals were taken from available tables of overlap integrals[3].

Table I summarizes the hybrids and the bond overlaps. 1,5,9-Tridehydro(12)annulene has only two nonequivalent carbons, and in all five different hybrid orbitals describe the molecule. The results show that hybrids differ appreciably from the corresponding *sp* and sp^2 forms adopted in simplified models when the exponent n in sp^n is restricted to the integers 1, 2 or 3. Thus, Φ_{21} and Φ_{23} which are described as sp^2 in the simple model, are very different. Hybrid Φ_{21} which is directed toward the CC double bond, has higher *s* content. Similarly, Φ_{32} and Φ_{34} are assumed to be *sp* hybrids

TABLE I

The Maximum Overlap Hybrids, the Bond Overlaps and the Angles of Deviation of Hybrids from the Bond Directions for 1,5,9-Tridehydro(12)annulene

1,5,9-Tridehydro(12)annulene

Hybrids		Overlaps
$\Phi_{12} = 0.60610\,(s) + 0.79539\,(p)$	$sp^{1.72}$	$S_{12} = 0.76408$
$\Phi_{23} = 0.56494\,(s) + 0.82513\,(p)$	$sp^{2.13}$	$S_{23} = 0.74584$
$\Phi_{32} = 0.67634\,(s) + 0.73659\,(p)$	$sp^{1.19}$	
$\Phi_{34} = 0.73659\,(s) + 0.67634\,(p)$	$sp^{0.84}$	$S_{34} = 0.85385$
$\Phi_{2H} = 0.55989\,(s) + 0.82857\,(p)$	$sp^{2.19}$	$S_{2H} = 0.74011$

Interorbital angle $\Theta_2^{1,3} = 121^0\,27'$

Deviation angle $\delta_{21} = \delta_{23} = 44'$

in the simple model, but the hybrids directed toward the short CC triple bond prefer higher *s* content.

The deviation angles found are very small, as could be expected. (In cyclic systems as a rule, bent bonds appear, but the deviation angles of 1^0 or 2^0 may be ignored). Since there are not significant deviation angles in the tridehydro(12)annulene investigated, a comparison with the results of calculations on several open-chain olefins and acetylenes or systems known to be highly strained, is of interest. In most of the computations on open chain olefins and acetylenes the experimental bond lengths were adopted. Here we used standard bond lengths, which may differ from the experimental by 0.02 Å. It is expected that this difference will not affect the hybrids much.

It may be of interest to establish to what extent the variations of the hybrids in otherwise similar suroundings are due to the variations of the CC bond lengths used in different calculations. We start the calculations by assuming a *standard* CC bond length. In particular, we select a CC bond suggested by Dewar and Schmeising. However, Dewar and Schmeising assume bond types characterised by *sp*, sp^2, and sp^3 hybrids, while the results of our calculations are sp^n hybrids, n being nonintegral, which leads to an inconsistency. We can eliminate this inconsistency by using the bond overlap -bond length correlation[4,5] and by repeating the calculation with the new bond lengths obtained from the overlap-length relationship until the assumed and the calculated bond lengths agree within the desired accuracy. The following are the standard bond lengths and the bond lengths which result from the application of the overlap-length relationship:

bond type		standard (ref. 2)	calculated
C—C	sp^2—sp	1.43 Å	1.428 Å*
C=C	sp^2—sp^2	1.32 Å	1.333 Å**

The bond overlap-bond length relationships are given by:

* C—C = $-\,1.166\,S_{CC} + 2.298$ (ref. 4)

** C=C = $-\,0.677\,S_{CC} + 2.087$ (ref. 5)

The difference between the two sets of bond lengths, or more precisely, the difference between the values of the corresponding basic atomic integrals, indicates the degree of the inconsistency in such calculations. As we see the difference is not large and should not cause concern.

Comparison with the experimental data: NMR spectra of 1,5,9-tridehydro (12)annulene are available and may be used for making comparisons with the computed *s-p* hybrid compositions using the established empirical correlations. Thus using the well known relationship of Muller and Pritchard[6]

$$J_{C^{13}—H} = 500\, a^2$$

between the spin-spin coupling constant for the C^{13}—H bond and the coefficient a, defining the hybrid CH, we predict for the spin-spin coupling 156.5 cps, while the experimental value is 169 cps[7]. A better value (162 cps) is obtained if we use the linear relationship:

$$J_{C^{13}—H} = 1079\, a^2/(1 + S^2) — 54.9$$

which takes into account variations in CH bond overlaps.

Chemical shifts have also been reported for the tridehydro(12)annulene. An attempt to correlate the hybrid exponents n calculated by the maximum overlap method and proton chemical shifts in hydrocarbons has been made[8]. A linear relationship:

$$\tau = 5\,(n — 1)$$

is obtained. Although lacking a theoretical justification it gives satisfactory results when applied to a number of molecules. For the olefinic protons in tridehydro(12)annulene it predicts $\tau = 5.95$, as compared to the experimental value[7] of 5.58. The agreement indicates that the tridehydro(12)annulene does not sustain diamagnetic currents, characteristic for aromatic systems, and that bonds in this system are well represented by a localised model. The relationship $\tau = 5\,(n — 1)$ is not valid for molecules with delocalized π-electrons because of the additional magnetic field due to ring currents which shifts the signal to either higher or lower fields, depending on the positions of the protons.

In spite of the limited comparison with experimental quantities, due to lack of experimental data, the results of the maximum overlap calculations are useful for comparisons between different molecules. We have seen that small variations in hybrid composition and in the magnitudes of various CC or CH bond overlaps can account for corresponding differences in the vicinity of the similar structural grouping. Thus they provide an adequate form for descriptions of not only widely different molecular species but also of structurally similar molecules for which the simple hybrids with the restriction that the hybrid exponent be an integer are not flexible enough.

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IZVOD

Hibridizacija u 1,5,9-tridehidro(12)anulenu

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Metodom maksimalnog prekrivanja izračunata je hibridizacija u 1,5,9-tridehidro(12)anulenu. Rezultati pokazuju da hibridi koji opisuju CC dvostruku vezu i CC trostruku vezu imaju više *s*-karaktera, nego hibridi istog ugljikovog atoma u jednostrukoj vezi. Prema tome, CC dvostruka i CC trostruka veza ojačane su ne samo s dodatnim π-tipom prekrivanja, nego i sa σ-tipom koji prati povećanje *s*-karaktera. Upotrebom postojećih empirijskih korelacija učinjena je usporedba između izračunatih i eksperimentalnih NMR podataka [spin-spin konstante sprezanja J (C^{13}—H) i kemijski pomak τ].

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