Hybridization in Fused Strained Rings by the Maximum-Overlap Method. I. Biphenylene and Benzo[1,2:4,5]dicyclobutene

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Abstract: Hybridization in biphenylene and benzo[1,2:4,5]dicyclobutene is considered by the method of maximum overlap. These molecules are highly strained, as evidenced by a large p content of the hybrids involved in CC bonds of the four-membered rings and their large deviation angles. A comparison between the experimental $J_{^{13}\text{C-H}}$ spin–spin coupling constants and calculated values based on the empirical Muller–Pritchard relationship, $J_{^{13}\text{C-H}} = 500a^2$, is made. The coefficient a of the carbon (2s) orbital, determined by the maximum-overlap method, gives a satisfactory agreement for a number of the highly strained hydrocarbons related to biphenylene and benzo[1,2:4,5]dicyclobutene. A correlation between bond overlaps and bond lengths for biphenylene indicates that contributions to CC bond lengths arising from variations in σ bonding may account for a better agreement between the calculated and experimental bond lengths, when superimposed to π contributions.

Hybridization, a local property of the wave function, is a useful concept for discussing many molecular properties including bond angles, bond lengths, spin–spin coupling constants, and, in certain cases, nuclear magnetic resonance shifts and force constants. Therefore, it is desirable to have the hybridization parameters for molecules with interesting structural groupings. However, the methods affording numerical characterization of hybridization are not unique, either because of ambiguous definition of hybridization or because of the limited reliability of predictions based on the semiempirical wave functions.[1] We considered the hybridization obtained by adopting a somewhat modified criterion of maximum overlapping, originally suggested by Slater and Pauling. The computations were not directly based on the variational theorem where the energy is minimized with respect to a set of parameters. Instead, a basis set consisting of local hybrid orbitals was assumed and parameters specifying the hybridization were varied in order to maximize a suitably weighted sum of bond overlaps.

In this paper we consider the hybridization in the structurally related and highly strained fused hydrocarbons biphenylene and benzo[1,2:4,5]dicyclobutene. One can expect that the hybrids describing CC bonds of the highly strained fused rings deviate considerably from the bond directions, forming thus the so-called bent bonds first suggested and discussed by Coulson and Moffitt[2] in cyclopropane. The hybridization of the carbon juncture atoms is particularly interesting since the simple description in terms of sp^2 hybrids is evidently not satisfactory. Namely, it has been suggested on the grounds of experimental work that these hybrids are significantly perturbed by fusion.[3] The chemical properties of several aromatic hydrocarbons having a fused strained ring have recently been examined and reported.[3–6]

Biphenylene and benzo[1,2:4,5]dicyclobutene are planar molecules which belong to the D_{2h} symmetry point group. Although both molecules have a four-membered ring fused to a six-membered ring, they are different enough to merit separate consideration.

The maximum-overlap method has already been applied to various polycyclic and small-ring hydrocarbons.[6–10] Briefly, in the maximum-overlap method one searches for optimal hybrid parameters a_i, b_i, of the individual hybrids

$$\psi_i = a_i(\text{s}) + b_i(\text{p}_i) \tag{1}$$

where s and p_i are 2s and 2p orbitals of the carbon atom, so that a suitably weighted sum of bond overlaps

$$S = k_{\text{CH}}\Sigma S_{\text{CH}} + k_{\text{CC}}\Sigma S_{\text{CC}} \tag{2}$$

has a maximum value. Here S_{CC} and C_{CH} represent bond overlaps of CC and CH bonds, respectively. The weighting factors $k_{\text{CH}} = 135.9$ and $k_{\text{CC}} = 121.2$ kcal mol^{-1} take into account the difference in energy of different bonds. The hybrid coefficients a_i and b_i are subject to orthonormality requirements

$$a_ia_j + b_ib_j \cos \vartheta_{ij} = \begin{cases} 0, & i \neq j \\ 1, & i = j \end{cases} \tag{3}$$

which ensure that the hybrids ψ_i and ψ_j at the same atom are normalized and mutually orthogonal. In cyclic systems, hybrids generally deviate from the internuclear lines. In these cases p orbitals are decomposed into the parallel and the perpendicular to the bond components

$$\text{p} = \cos \delta(\text{p}_{\parallel}) + \sin \delta(\text{p}_{\perp}) \tag{4}$$

Here δ denotes the deviation of the hybrid from the internuclear vector. The maximum of expression 2 is found by a numerical trial and error procedure. One starts with assumed initial hybrid compositions, *e.g.*, sp^3, sp^2, or sp hybrids, and then by a systematic variation of all independent parameters approaches the optimal values. For each molecule a Fortran IV program

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was written, where the independent hybridization ratios $(b_i/a_i)^2$ are varied in steps of ± 0.1 first and later in steps ten times smaller. There are a relatively large number of independent parameters ratios $(b_i/a_i)^2$ to be optimized (six in biphenylene and five in benzo[1,2:4,5]dicyclobutene). In addition, the relative orientation of the hybrids toward the molecular skeleton, *i.e.*, the magnitudes of the deviation angles δ, need to be found for any assumed hybridization. A simultaneous variation of all these parameters would be time consuming. However, the hybrids at a single atom do not strongly depend on the assumed hybridization in the neighboring atoms and consequently the parameters can be varied successively. When the best parameters are determined by the first iteration, the whole procedure is repeated until the input and the output hybrid ratios are equal to three figures. Further, we assumed that the deviation angles at carbon atoms 5 and 6 are equal ($\delta_{54} = \delta_{56}$, $\delta_{65} = \delta_{61}$). This is not a severe restriction since these deviation angles are expected to be very small.

Biphenylene and benzo[1,2:4,5]dicyclobutene are examples of the strained molecules which have hybrids inclined toward the inside of a ring; *i.e.*, the deviation angles are *negative*. Namely, the hybrids of the highly strained four-membered ring are expected[11] to have deviation angles of about 10° and consequently they are directed toward the inside of the benzene ring. The situation is unlike what is usually met in nonplanar polycyclic systems. For example, in nortricyclene,[9] benzvalene, and prismane,[6] etc., the relief of the strain in the small rings is achieved by allowing the hybrids to point *outside the planes* of the three-membered rings, while being at the same time *outside* the larger rings. In a hypothetical planar 1,3,5-cycloheptatriene the hybrids would point toward the inside of the ring. However, puckering of the molecular skeleton increases the CC bond overlaps leading thus to the more favorable nonplanar geometry of the molecule.[12] Therefore, it is of considerable interest to find the amount of the negative hybrid deviation in molecules like biphenylene and benzo[1,2:4,5]dicyclobutene.

Biphenylene. The bond lengths and bond angles reported recently by Fawcett and Trotter[13] were adopted. The unusual feature of the experimental findings is the long C_1–C_7 bond (1.514 Å) and the relatively short C_1–C_6 bond (1.372 Å). The basic overlap integrals for various CC and CH bonds used in the calculation are given in Table I. They are based on "double ζ" type atomic orbitals of Clementi.[14] Although Clementi orbitals were recommended for molecular calculations, they are in fact appropriate for free atoms. It is now known that the screening constants of the atomic orbitals are quite different in molecules. Furthermore, screening constants can vary for different carbons in a compound. Thus, the number of significant figures given in the tables of overlap integrals[15] is greater than the method warrants and the numbers were rounded to three figures.

The maximum-overlap hybrids, bond overlaps, and interorbital and deviation angles are listed in Table II.

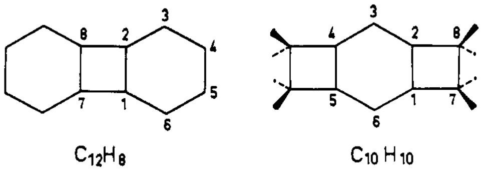

Figure 1. Schematic diagrams and numbering of atoms for diphenylene and benzo[1,2:4,5]dicyclobutene. The unusual numbering in biphenylene is adopted in order to facilitate a comparison of hybrids between the two molecules.

The hybridization at carbon 1 is of particular interest. The deviation angle $\delta_{17} = 17.5°$ is the largest deviation angle found in the four-membered rings. It contributes to the weakening of the C_1–C_7 bond. The hybrids ψ_{16} and ψ_{61}, which describe C_1–C_6 σ bond, have considerably different deviation angles: δ_{16} is about 7°, while δ_{61} is almost zero. We may describe this case as a *half-bent* or *semibent* bond, because it is halfway between a straight and a bent bond. It is worthwhile to indicate the kinds of the chemical bonds in hydrocarbons: bent bonds,[2] bent-out-of-plane bonds as found, *e.g.*, in prismane,[6] and twisted bonds where hybrid directions and the internuclear vector do not lie in the same plane.[16,17] (There is yet another possible type of bond where the hybrids are on the opposite sides of the internuclear line: *i.e.*, the deviation angles δ_{ij} and δ_{ji} are of the opposite sign. Therefore, it is called an antibent bond. This type of bonding occurs in the C_5–C_6 bond of biphenylene, where the corresponding deviation angles are $\delta_{65} = 2.9°$ and $\delta_{56} = -0.4°$.)

In spite of the inefficient overlapping, the half-bent bond C_1–C_6 does lead to a large bond overlap. This is mainly due to a relatively short bond length and a very high s content of the ψ_{16} hybrid.

Benzo[1,2:4,5]dicyclobutene. Bond lengths and the bond angles for benzo[1,2:4,5]dicyclobutene were taken from X-ray measurements recently reported by Lawrence and MacDonald.[18] The numbering system used for this molecule is shown in Figure 1. Bond lengths deviate from the values usually met in condensed benzene rings and fused four-membered rings. For instance, the C_1–C_2 bonds is unusually short, $d(C_1$–$C_7) = 1.35$ Å, while the C_7–C_8 bond is unexpectedly long, $d(C_7$–$C_8) = 1.56$ Å. We have adopted these bond lengths and used the appropriate basic overlap integrals cited in Table I. The maximum overlap hybrids, bond overlaps, and interorbital and deviation angles are listed in Table II. The deviation angles at the carbon 1 are all approximately equal in magnitude, unlike the case of biphenylene. Since the deviation angle δ_{61} is different from zero, there is no semibent bond. The hybrids, bond overlaps, and deviation angles at carbon 7 are similar to those found in cyclobutene.[11] It has to be noticed that hybrids ψ_{78} and ψ_{87} have very high p character. This is consistent with the observed increase in the C_7–C_8 bond length. A linear relationship between the bond lengths and bond overlaps in molecules characterized by straight or bent bonds with small

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Table I. The Basic Overlap Integrals for Clementi "Double ζ" Atomic Wave Functions for CC and CH Bonds in Biphenylene and Benzo[1,2:4,5]dicyclobutene[a]

	CC bonds, Å						CH bonds, Å		
	Biphenylene								
	1–2	1–7	1–6	5–6	5–4				
	1.43	1.54	1.37	1.42	1.39				1.060
(2s, 2s)	0.405	0.357	0.433	0.410	0.423		(1s, 2s)		0.587
(2s, 2p)	0.447	0.415	0.462	0.449	0.457		(1s, 2p)		0.509
(2p, 2p)$_{\parallel}$	0.256	0.275	0.242	0.254	0.247				
(2p, 2p)$_{\perp}$	0.306	0.265	0.330	0.340	0.322				
	Benzo[1,2:4,5]dicyclobutene								
						7–8		6–H	7–H
	1.35	1.50	1.38			1.56		1.084	1.092
(2s, 2s)	0.442	0.374	0.428			0.348	(1s, 2s)	0.575	0.571
(2s, 2p)	0.467	0.427	0.460			0.409	(1s, 2p)	0.506	0.505
(2p, 2p)$_{\parallel}$	0.236	0.269	0.244			0.277			
(2p, 2p)$_{\perp}$	0.338	0.279	0.326			0.258			

[a] The experimental bond lengths of ref 13 and 18 are assumed (rounded to the nearest 0.01 Å for CC and 0.002 Å for CH bonds, respectively.

Table II. Calculated Maximum Overlap Hybrids, Bond Overlaps, Interhybrid Angles, and Angles of Hybrid Deviations from the Internuclear Line[a]

Hybrids	Bond overlaps	Interhybrid angles, deg	Deviation angles, deg
	Biphenylene		
$\psi_{12} = sp^{2.36}$	$S_{12} = 0.706$	$\vartheta_1^{26} = 122.1$	$\delta_{12} = -7.9$
$\psi_{16} = sp^{1.50}$	$S_{16} = 0.757$	$\vartheta_1^{67} = 122.5$	$\delta_{16} = 7.4$
$\psi_{17} = sp^{2.31}$	$S_{17} = 0.663$		$\delta_{17} = 17.5$
$\psi_{61} = sp^{1.89}$			$\delta_{61} = 2.8$
$\psi_{65} = sp^{2.03}$			$\delta_{56} = -0.4$
	$S_{56} = 0.730$		
$\psi_{56} = sp^{1.96}$		$\vartheta_5^{46} = 121.5$	
$\psi_{54} = sp^{1.87}$	$S_{54} = 0.744$		
$\psi_{5H} = sp^{2.19}$	$S_{5H} = 0.751$		
$\psi_{6H} = sp^{2.10}$	$S_{6H} = 0.753$	$\vartheta_6^{15} = 120.8$	
	Benzo[1,2:4,5]dicyclobutene		
$\psi_{12} = sp^{2.03}$ $\psi_{16} = sp^{1.68}$	$S_{12} = 0.739$	$\vartheta_1^{26} = 122.8$	$\delta_{12} = -9.9$
	$S_{16} = 0.747$	$\vartheta_1^{67} = 120.1$	$\delta_{16} = 6.7$
$\psi_{61} = sp^{1.96}$			$\delta_{61} = 6.3$
$\psi_{17} = sp^{2.38}$			$\delta_{17} = 13.2$
	$S_{17} = 0.665$	$\vartheta_7^{18} = 107.2$	
$\psi_{71} = sp^{3.23}$			$\delta_{71} = 11.2$
$\psi_{78} = sp^{3.56}$	$S_{78} = 0.626$		$\delta_{78} = 9.9$
$\psi_{6H} = sp^{2.08}$	$S_{6H} = 0.743$		
$\psi_{7H} = sp^{2.68}$	$S_{7H} = 0.728$		

[a] ψ_{ij} and ψ_{iH} are hybrid orbitals centered on carbon atom i and directed toward a carbon atom j or a hydrogen atom, respectively. ϑ_i^{jk} is the angle between the directions of the hybrids ψ_{ij} and ψ_{ik}. The deviation is designated by δ_{ij}.

deviations of a few degrees has been established.[19] However, this relationship is obscured in highly strained molecules by the presence of large deviation angles. Therefore, in fused strained hydrocarbons we can expect only a consistency between the changes in bond lengths and bond overlaps. It was noticed that the C_7–C_8 bond length is in agreement with the magnitude of the bond overlap, while there is no simple explanation of the shortening of C_1–C_7 bond to 1.50 Å (the sp^3–sp^2 single CC bond is, according to Dewar and Schmeising,[20] 1.520 Å). Similarly, the shortening of the C_1–C_2 bond to 1.35 Å cannot be explained by simple overlap arguments. These discrepancies may perhaps be caused by other effects, *e.g.*, by a considerable perturbation of the π-electron system produced by fusion of the highly strained small ring.

Discussion

Several maximum overlap parameters, in particular the hybrid s characters and bond overlaps, have been correlated with various experimental quantities, such as CC bond energies and vibrational frequencies,[11] chemical shifts,[6] $J_{^{13}\mathrm{C-H}}$ and $J_{^{13}\mathrm{C-}^{13}\mathrm{C}}$ spin–spin coupling constants,[21] CH and CC bond lengths,[19] and proton acidities.[22] There are not many experimental data to be correlated with hybridization in biphenylene and benzo[1,2:4,5]bicyclobutene. The $J_{^{13}\mathrm{C-H}}$ coupling constants, according to current assumptions, provide a direct measure of the s character of the hybrids describing CH bonds.[23] Unfortunately, $J_{\mathrm{C^{13}-H}}$ has not been reported for molecules considered in this paper. Instead, there is a value $J_{^{13}\mathrm{C-H}} = 138$ cps[24] found in related benzocyclobutene. Since the maximum-overlap method reflects the local properties of the molecules, we can expect that the hybridization of the carbon atom 7 in benzo[1,2:4,5]dicyclobutene is very close to that in benzocyclobutene. By using the Muller–Pritchard relationship

$$J_{^{13}\mathrm{C-H}} = 500a^2 \text{ cps} \qquad (5)$$

where a is the coefficient of the carbon (2s) orbital of the hybrid describing the CH bond in question, a comparison was made between the experimental and calculated ^{13}C–H coupling constants for several highly strained hydrocarbons containing four-membered rings (Table III). The empirical relationship 5 does not assume any particular method of calculation of the hybridization parameters. Therefore, the obtained agreement illustrated in Table III gives a strong indication that the maximum-overlap method is a suitable tool for the evaluation of the hybridization in these molecules.

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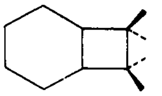
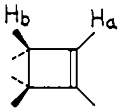
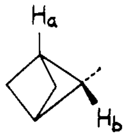
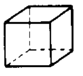
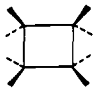
Table III. A Comparison between the Experimental and Calculated $J_{^{13}C-H}$ Spin–Spin Coupling Constants for Several Cyclic and Polycyclic Hydrocarbons[a]

	$J_{^{13}C-H}$(exptl)	Ref	$J_{^{13}C-H}$(calcd)	Ref
	138	24	135.7	*b*
	H_a 170	*c*	177.0	11
	H_b 140		139.5	
	H_a 164	*d*	160.7	8
	H_b 144		144.5	
	160 ± 5	*e*	160.5	8
	134	*f*	138.1	*g*

[a] The coefficient *a*, used in the Muller–Pritchard relationship, $J_{^{13}C-H} = 500a$, was obtained by the maximum-overlap method. [b] Calculated for benzo[1,2:4,5]dicyclobutene. [c] S. Borčić and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 1056 (1965); revised by E. A. Hill and J. D. Roberts, *ibid.*, **89**, 2047 (1967). [d] K. B. Wiberg, G. M. Lapman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965). [e] P. E. Eaton and T. W. Cole, *J. Amer. Chem. Soc.*, **86**, 962 (1964). [f] C. S. Foote, *Tetrahedron Lett.*, 579 (1963).

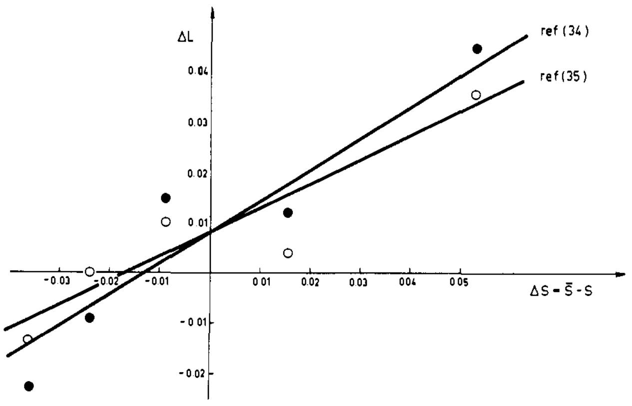


Figure 2. Plot of the difference between experimental and calculated bond lengths against the difference between the mean overlap value and the corresponding bond overlap. Results of ref 28 and 29 are represented by full and open circles, respectively.

Table IV. Experimental and Calculated Bond Lengths in Biphenylene and a Comparison between Their Difference and the Difference of the *Mean* CC Bond Overlap ($\bar{S}$) and the Bond Overlap in Question

	Bond lengths			Exptl − calcd			
	Exptl	Calcd[a]	Calcd[b]	*a*	*b*	S	$\bar{S} - S$
C_1–C_7	1.514	1.467	1.476	0.047	0.038	0.667	0.053
C_1–C_2	1.426	1.414	1.422	0.012	0.004	0.702	0.018
C_1–C_6	1.372	1.395	1.385	−0.023	−0.013	0.756	−0.036
C_5–C_6	1.423	1.408	1.413	0.015	0.010	0.729	−0.009
C_4–C_5	1.385	1.394	1.385	−0.009	0.000	0.744	−0.024

[a] Reference 28. [b] Reference 29.

Finally, we wish to examine the extent to which the calculated bond overlaps can be correlated with the experimental bond lengths. Bond overlaps provide a measure of the electronic overlap density in the region between the bonded atoms. Therefore, they are expected to present a suitable bond index, especially if the bond is largely covalent. The environmental variations in CC single bonds, originating from the differences in hybridization of carbon atoms,[20,25,26] have led to the linear relationship between bond overlaps and bond lengths[19] which may be applied to general sp^n hybrids (n is not restricted to integers 1, 2, 3). A similar correlation is found for CC double bonds.[27] However, the situation is more complicated in molecules with delocalized π electrons which also contribute to CC bond-length variations. Several attempts were made to ascribe these variations solely to the changes in π-electron bond orders obtained by MO methods at various levels of sophistication. The results have not only shown a disagreement with experimental bond lengths for a large number of molecules but also indicate considerable variation in predicted bond lengths when different modifications of the MO method were applied to the same molecule. We shall discuss in detail two MO-type calculations performed on biphenylene.[28,29] The calculated CC bond lengths by these two methods are compared with experimental ones in Table IV. The question arises whether the changes in hybridization, when taken into account, can remove the observed discrepancy in Table IV. Unfortunately, we do not know the relative weights of the σ and π contributions to the variations in bond lengths. Therefore, we can only compare the changes in σ-bond overlaps with the differences between the experimental and calculated (using π electrons only) bond lengths. This correlation is presented in Figure 2. The observed linear relationship is fairly good. It has to be pointed out that this correlation is based on the completely *unrelated* methods of calculation. Namely, the maximum-overlap approximation applied to the σ skeleton of the molecule neglects the contributions of π electrons, while the MO methods used were restricted to π electrons only, assuming a frozen σ framework. This result is promising for bond-length calculations, since it indicates that consideration of σ and π contributions to the CC bond lengths may account for their experimentally observed variations.

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