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Note

Hybridization in Fused Strained Rings by Maximum Overlap Method. III. Benzocyclobutadiene and Benzocyclobutene-7,8-dimethylene[1,2]

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The hybridization in benzocyclobutadiene and benzocyclobutene-7,8-dimethylene is considered using the method of maximum overlap. The results show considerable variations of s—p content of hybrids describing the molecular skeleton. Endocyclic and exocyclic double bond in four-membered rings in these molecules exhibit values of deviation angles and bond overlap integrals differing from those in other examined fused ring molecules[1,2]. The calculated J(C—H) spin-spin coupling constants are in very good agreement with the available experimental data.

This work is the continuation of a study of fused ring systems initiated by the work on biphenylene, benzo(1,2:4,5)dicyclobutene, benzocyclobutene and benzocyclopropene[1,2]. All these molecules are homologues of indane and are of great interest to chemists. For this reason organic chemists try to sintetize them. In this series of molecules only benzocyclobutadiene has not yet been isolated. Theoretical calculation of its electronic structure may account for its instability. These molecules characterized by fused rings have extremely unusual geometrical angles forced by in-plane fusion of already strained rings. The fusion of rings does not allow all hybrids to adopt simultaneously the most favorable orientation *with respect to* the molecular skeleton. For this reason simple description in terms of sp^2 or sp^3 hybrides is not adequate for these molecules. Better description of fused ring systems is obtained by the application of the maximum overlap method, in which hybrids are of the form sp^n, where n is not restricted to the integers 1, 2, and 3.

The maximum overlap type of calculation has recently been appliad to a large number of hydrocarbons and has been described in literature[3–5]. Briefly, we search for the optimal parameters a_i, b_i, *i. e.* exponent n_i, for hybrids of all carbon atoms in the molecule which maximize the sum, over all bonds, of the suitably scaled bond overlaps. The best hybrid parameters are obtained by systematic variation of all independent parameters.

RESULTS AND DISCUSSION

The molecules are assumed to be planar[6] and standard bond lengths for hydrocarbons, suggested dy Dewar and Schmeising[7], have been adopted. Clementi double zeta orbitals[8] were utilized and the values of basic overlap integrals were taken from available tables[9]. The molecular geometry and numbering of atoms are shown in Fig. 1.

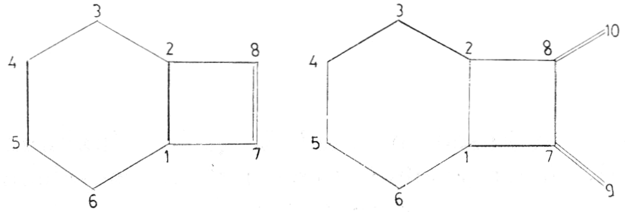

Fig. 1. Schematic diagrams and numbering of atoms for benzocyclobutadiene and benzocyclobutene-7,8-dimethylene

TABLE I

Calculated Maximum Overlap Hybrids, Bond Overlaps, Interhybrid Angles, and Angles of Hybrids Deviations from the Internuclear Line

Hybrids	Bond overlaps	Interhybrid angles	Deviation angles
	Benzocyclobutadiene		
$\varphi_{12} = sp^{2.391}$	$S_{12} = 0.7108$	$\vartheta_1^{26} = 120.9^\circ$	$d_{12} = -8.2^\circ$
$\varphi_{17} = sp^{2.145}$	$S_{17} = 0.6923$	$\vartheta_1^{67} = 122.9^\circ$	$d_{17} = 19.1^\circ$
$\varphi_{71} = sp^{1.920}$		$\vartheta_7^{18} = 125.8^\circ$	$d_{71} = 17.4^\circ$
$\varphi_{16} = sp^{1.589}$	$S_{16} = 0.7424$		$d_{16} = 9.2^\circ$
$\varphi_{61} = sp^{1.994}$		$\vartheta_6^{15} = 121.8^\circ$	$d_{61} = 0.9^\circ$
$\varphi_{65} = sp^{1.804}$	$S_{56} = 0.7393$		$d_{65} = 0.9^\circ$
$\varphi_{56} = sp^{1.916}$		$\vartheta_5^{46} = 121.5^\circ$	$d_{54} = 0.7^\circ$
$\varphi_{78} = sp^{1.520}$	$S_{78} = 0.7624$		$d_{78} = 17.2^\circ$
$\varphi_{5H} = sp^{2.186}$	$S_{5H} = 0.7402$		
$\varphi_{6H} = sp^{2.232}$	$S_{6H} = 0.7392$		
$\varphi_{7H} = sp^{2.836}$	$S_{7H} = 0.7276$		
	Benzocyclobutene-7,8-dimethylene		
$\varphi_{12} = sp^{2.435}$	$S_{12} = 0.7093$	$\vartheta_1^{26} = 120.4^\circ$	$d_{12} = -7.3^\circ$
$\varphi_{17} = sp^{2.080}$	$S_{17} = 0.6870$	$\vartheta_1^{67} = 123.2^\circ$	$d_{17} = 17.6^\circ$
$\varphi_{71} = sp^{2.418}$		$\vartheta_7^{18} = 114.9^\circ$	$d_{71} = 14.4^\circ$
$\varphi_{16} = sp^{1.603}$	$S_{16} = 0.7454$		$d_{16} = 7.7^\circ$
$\varphi_{61} = sp^{1.910}$		$\vartheta_6^{15} = 122.0^\circ$	$d_{61} = 1.0^\circ$
$\varphi_{65} = sp^{1.863}$	$S_{65} = 0.7404$		$d_{65} = 1.0^\circ$
$\varphi_{56} = sp^{1.916}$		$\vartheta_5^{46} = 121.5^\circ$	$d_{54} = 0.7^\circ$
$\varphi_{78} = sp^{2.326}$	$S_{78} = 0.6901$		$d_{78} = 12.0^\circ$
$\varphi_{79} = sp^{1.458}$	$S_{79} = 0.7732$		
$\varphi_{97} = sp^{1.706}$			
$\varphi_{H5} = sp^{2.189}$	$S_{5H} = 0.7401$		
$\varphi_{6H} = sp^{2.256}$	$S_{6H} = 0.7388$		
$\varphi_{9H} = sp^{2.172}$	$S_{9H} = 0.7405$		

Benzocyclobutadiene and benzocyclopropene-7,8-dimethylene have 4 and 5 nonequivalent carbon atoms, respectively, which lead to 8 and 10 independent hybrids. Since the number of independent parametars is large, we assumed that the deviation angles d at benzene carbons C_5, and C_6, $d_{65}=d_{61}$ and $d_{54}=d_{56}$, are equal in both molecules considered in this paper.

The results of MOA calculations are presented in Table I. where hybrids are cited in the sp^n notation (n is defined by $n = (1 - a_{ij}^2)/a_{ij}^2$, where a_{ij}^2 is the s-character of the corresponding hybrid φ_{ij}).

Inspection of the Table I reveals that exo- and endodouble bond of four member rings in benzocyclobutene-7,8-dimethylene and benzocyclobutadiene are more strained than the corresponding bonds in biphenylene and benzo(1,2:4,5)dicyclobutene[1]. The values of bond overlaps of the benzene ring are smaller, while the deviation angles are greater, which means that these molecules are less stable than biphenylene and benzo(1,2:4,5)dicyclobutene, as far as σ-framework is concerned. This increased instability due to angular strain is further increased in benzocyclobutadiene by the antiaromaticity of its π-system. This is in accordance with experimental evidence since all attempts to prepare and synthetize this compound failed so far[12,13]. The calculated REPE (resonance energy per π electron)[14] shows clearly that benzocyclobutadiene has antiaromatic character while, for instance, biphenylene is an aromatic molecule.

The calculated J(C—H) spin-spin coupling constants are compared with the available experimental data in Table II.

The semiempirical formula of Maksić *et al.*[15] gives a very fine agreement with experiment for benzocyclobutene-7,8-dimethylene. The experimental values of J(C—H) coupling constants are not known in benzocyclobutadiene. We

TABLE II

A Comparison between Experimental and Calculated
$J_{C^{13}-H}$ Spin-Spin Coupling Constants

	Muller* and Prichard	Modified** expresion	Experiment
	Benzocyclobutadiene		
H_5	156.9	159,4	158.7 ± 0.8[a]
H_6	154.7	156,6	
H_7	130.4	129,1	
	Benzocyclobutene-7,8-dimethylene		
H_5	156.8	159,2	158.7 ± 0.8[a]
H_6	153.7	154,9	
H_9	157.6	160.4	~160[b]

* N. Muller and D. E. Prichard, *J. Chem. Phys.*, **31** (1969) 768, 1471.

** Z. B. Maksić, *Int. J. Quant. Chem.*, **S5** (1971) 301; Z. B. Maksić, M. Eckert-Maksić and M. Randić, *Theor. Chim. Acta*, **22** (1971) 70.

[a] J. W. Emsley, J. Feeny and L. H. Sutcliffe, *High Resolution N.M.R. Spectroscopy*, vol. 2, Pergamon Press, Oxford, 1966, p. 1023, the value shown is for benzene;

[b] V. M. Gil, *Nato Summer School on N.M.R. Spectroscopy*, Coimbra-Portugal, September 1968 p. 39, the value shown is for $=CH_2$ group.

compare the J (C—H) constant at the site C_5 with the value found in benzene. The formula of Maksić *et al.*[15] yields the value which is within the limits of the experimental errors.

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SAŽETAK

Hibridizacija u spojenim prstenovima metodom maksimalnog prekrivanja. III. Benzociklobutadien i benzociklobuten-7,8-dimetilen

Lj. Vujsić

Izračunana je hibridizacija u benzociklobutadienu i benzociklobutenu-7,8-dimetilenu. Rezultati pokazuju znatnu razliku u s-p karakteru hibrida koji opisuju kostur molekula. Endociklična ili eksociklična dvostrusa veza četvoročlanih prstenova ovih molekula uslovljava druge vrednosti devijacionih uglova i integrala prekrivanja nego u drugim, do sada ispitanim molekulima, sa spojenim prstenovima. Izračunane J(C—H) konstante sprezanja spinova su u vrlo dobrom slaganju sa raspoloživim eksperimentalnim podacima.

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