Hybridization in 1,3,5-Cycloheptatriene and Some Related Molecules by the Method of Maximum Overlap

Z. Meić and M. Randić

Institute »Ruđer Bošković«, Zagreb, Croatia, Yugoslavia

The hybridization in 1,3,5-cycloheptatriene, 1,3,5,7-cyclooctatetraene, 1,3-cyclohexadiene, and 1,4-cyclohexadiene has been calculated by the method of maximum overlap. The results show that if the molecules are assumed to be planar, hybrids describing the molecular skeleton deviate from the line joining the neighbouring carbon atoms and are directed towards the inside of the ring. The deviation angles for the above molecules vary between 1.25⁰ and 7.5⁰. For non-planar structures the deviation angles are decreased or are equal to zero. The puckering of the molecular skeleton thus considerably reduces the strain.

INTRODUCTION

Although different molecular parameters are reported[1,2] for 1,3,5-cycloheptatriene there is no doubt that the nonplanarity of the carbon skeleton is very pronounced, and that the carbon atoms are far from being in the same plane, as believed a decade ago[3]. It has been suggested[1] that the nonplanarity may have its origin in the interaction of the π-electrons, the energy of which will increase if the distance between C_1 and C_6 is decreased (Fig. 1a).
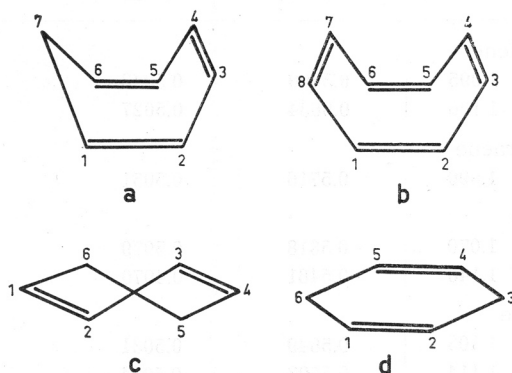

Fig. 1. Schematic diagrams of molecular geometries and the numbering of atoms for: (a)1,3,5--cycloheptatriene, (b)1,3,5,7-cyclooctatetraene, (c)1,3-cyclohexadiene, and (d)1,4-cyclohexadiene.

This forces the methylene group out of the plane formed by the $C_1C_2C_5C_6$ carbon atoms. In this paper we wish to examine the role that σ-skeleton may play, and for that purpose we calculate the best hybrids for the molecule by the method of maximum overlap. Clearly, if the molecule would be planar

the CCC valence angles cannot take their usual values: 120⁰ at carbon atoms of double bonds assumed sp^2 hybridized, and 109⁰ 28′ at the sp^3 hybridized methylene carbon. The deviation of the hybrids from the line joining bonded atoms will be towards the *inside* the ring, and the ring will assume a puckered form.

TABLE I

The Basic Atomic Overlap Integrals for Different CC and CH Bonds Found in the Molecules Investigated

Bond	Length (Å)	(2s, 2s)	(2s, 2p)	$(2p, 2p)_\sigma$	$(2p, 2p)_\pi$
1,3,5-Cycloheptatriene					
$C_1—C_2$	1.355	0.4398	0.4660	0.2372	0.3363
$C_2—C_3$	1.445	0.3983	0.4426	0.2596	0.2998
$C_1—C_7$	1.505	0.3718	0.4257	0.2702	0.2773
1,3-5,7-Cyclooctatetraene					
C=C	1.335	0.4493	0.4707	0.2311	0.3449
C—C	1.460	0.3916	0.4385	0.2626	0.2941
1,3-Cyclohexadiene					
$C_1—C_2$	1.340	0.4469	0.4695	0.2326	0.3427
$C_2—C_3$	1.470	0.3871	0.4357	0.2644	0.2903
$C_4—C_5$	1.495	0.3761	0.4286	0.2687	0.2810
$C_5—C_6$	1.510	0.3696	0.4243	0.2710	0.2755
1,4-Cyclohexadiene					
C = C	1.335	0.4493	0.4707	0.2311	0.3449
C — C	1.495	0.3761	0.4286	0.2687	0.2810

Bond	Lenght (Å)	(1s, 2s)	(1s, 2p)
1,3,5-Cycloheptatriene			
$C_1—H$	1.095	0.5690	0.5043
$C_7—H$	1.106	0.5634	0.5027
1,3,5,7-Cyclooctatetraene			
C—H	1.090	0.5716	0.5051
1,3-Cyclohexadiene			
$C_1—H$	1.070	0.5818	0.5079
$C_5—H$	1.140	0.5461	0.4970
1,4-Cyclohexadiene			
$C_1—H$	1.103	0.5649	0.5031
$C_3—H$	1.114	0.5593	0.5014

By the method of maximum overlap one searches for each carbon atom in the molecule hybrids of the general form sp^n, where n need not be an integer. The criterion used requires that orbitals involved in bond formation will contribute in an optimal way suitably weighted overlaps. For a detailed description of the method see refs. (4) and (5). We use Clementi functions for the

description of atomic orbitals[6] and the values reported by Treattenberg[1] for the C—C and C—H bond distances. The basic overlap integrals given in Table I are obtained by interpolation from published tables of overlap integrals for Clementi orbitals[7]. The scaling factors, introduced to reduce the different overlaps to energy are, as described previosly[5], $k_{CC} = 121.17$ and $k_{CH} = 135.86$.

RESULTS AND DISCUSSION

Besides the results for 1,3,5-cycloheptatriene we also include the results of maximum overlap hybridization for 1,3,5,7-cyclooctatetraene, 1,3-cyclohexadiene and 1,4-cyclohexadiene. For all these molecules, except the last one, a significant puckering of the ring skeleton is observed. A comparison between them will show whether the degree of the nonplanarity is consistent with the bond overlaps, hybrid composition and deviation angles of these molecules obtained by the maximum overlap method.

We calculated hybridization for experimentally observed geometry and for an assumed planar structure. For 1,3,5-cycloheptatriene hypothetical planar structure we arbitrarily assumed the CCC angle at the methylene group to be 120⁰ (usual value is close to 110⁰), and other CCC angles to be 130⁰ (usual value 120⁰). The best overlap is obtained when hybrids deviate from the line joining the neighbouring carbon atoms by $\delta = -4^0$, i. e. they are directed towards the inside of the ring. All interorbital angles are therefore approximately reduced by 8⁰, and are close to the usual CCC bond angles in acyclic systems. Since $\delta \neq 0$ we may associate with the system some strain energy, in the same way as we do with bent bonds in cyclopropane or cyclobutane. However in this case the strain of the hypothetical planar structure can be relieved by puckering the ring. The results using experimental data show that in this case the best hybrids are obtained when $\delta \sim 0$, which fully confirms our expectations (Table II). It is true that in the former case the total molecular overlap (the sum of all bond overlaps) is somewhat larger. However the bond lengths and the bond angles for the planar model, though plausible, have been arbitrarily assumed, and for this reason the theoretical results may not be appropriate for a detailed comparison with the real molecule.

We also include in Table II the results for 1,3,5,7-cyclooctatetraene, 1,3-cyclohexadiene and 1,4-cyclohexadiene. The calculations are made for the reported experimentally determined geometry, the bond lengths and bond angles which are based on electron diffraction measurements[8-10]. The best hybrids for 1,3,5,7-cyclooctatetraene are obtained when $\delta = -2^0$. This value should be compared to $\delta = -7.5^0$, required by the planar model assuming sp^2 hybrids. Thus again the puckering of the molecular skeleton will considerably reduce the strain.

The structure of 1,3-cyclohexadiene has several interesting features. The degree of the nonplanarity of skeleton depends on the relative importance of resonance and steric strain. The C_2 symmetry of the equilibrium conformation is found experimentally[9,11,12], the ethylene groups $(C_1C_2C_3C_6)$ are planar; and the two ethylene planes make an angle[9] of 17⁰. Bond angles, within the accuracy of the measurement, do not deviate from expectations based on existing experimental evidence, except the H—C—H angle in the methylene groups, which is unexpectedly small[9]. The results of the maximum overlap

TABLE II

The Maximum Overlap Hybrids, Exponent n *in the Notation* sp^n, *and Bond Overlaps for the Molecules Investigated*

Bond	Hybrid	n	Bond Overlap
1,3,5-Cycloheptatriene			
C_1—C_2	$\psi_{12} = 0.6000$ (s) $+ 0.8000$ (p)	1.777	$S_{12} = 0.7644$
	$\psi_{21} = 0.6254$ (s) $+ 0.7803$ (p)	1.557	
C_2—C_3	$\psi_{23} = 0.5862$ (s) $+ 0.8102$ (p)	1.910	$S_{23} = 0.7173$
	$\psi_{32} = 0.5476$ (s) $+ 0.8367$ (p)	2.334	
C_3—C_4	$\psi_{34} = 0.5884$ (s) $+ 0.8086$ (p)	1.889	$S_{34} = 0.7507$
	$\psi_{43} = \psi_{34}$		
C_1—C_7	$\psi_{17} = 0.5598$ (s) $+ 0.8287$ (p)	2.192	$S_{17} = 0.6858$
	$\psi_{71} = 0.5179$ (s) $+ 0.8555$ (p)	2.728	
C_1—H	$\psi_{1H} = 0.5716$ (s) $+ 0.8206$ (p)	2.061	$S_{1H} = 0.7390$
C_2—H	$\psi_{2H} = 0.5150$ (s) $+ 0.8572$ (p)	2.770	$S_{2H} = 0.7253$
C_3—H	$\psi_{3H} = 0.5949$ (s) $+ 0.8038$ (p)	1.825	$S_{3H} = 0.7439$
C_7—H	$\psi_{7H} = 0.4815$ (s) $+ 0.8765$ (p)	3.314	$S_{7H} = 0.7118$
1,3,5,7-Cyclooctatetraene			
C=C	$\psi_{12} = 0.6136$ (s) $+ 0.7896$ (p)	1.656	$S_{12} = 0.7692$
	$\psi_{21} = \psi_{12}$		
C—C	$\psi_{18} = 0.5679$ (s) $+ 0.8231$ (p)	2.100	$S_{18} = 0.7139$
	$\psi_{81} = \psi_{18}$		
C—H	$\psi_{CH} = 0.5486$ (s) $+ 0.8361$ (p)	2.323	$S_{CH} = 0.7358$
1,3-Cyclohexadiene			
C_1—C_2	$\psi_{12} = 0.5901$ (s) $+ 0.8073$ (p)	1.872	$S_{12} = 0.7604$
	$\psi_{21} = 0.6097$ (s) $+ 0.7926$ (p)	1.690	
C_2—C_3	$\psi_{23} = 0.5621$ (s) $+ 0.8271$ (p)	2.165	$S_{23} = 0.7083$
	$\psi_{32} = \psi_{23}$		
C_4—C_5	$\psi_{45} = 0.5418$ (s) $+ 0.8405$ (p)	2.407	$S_{45} = 0.6839$
	$\psi_{54} = 0.5179$ (s) $+ 0.8555$ (p)	2.728	
C_5—C_6	$\psi_{56} = 0.5179$ (s) $+ 0.8555$ (p)	2.728	$S_{56} = 0.6733$
	$\psi_{65} = \psi_{56}$		
C_1—H	$\psi_{1H} = 0.5985$ (s) $+ 0.8011$ (p)	1.792	$S_{1H} = 0.7551$
C_2—H	$\psi_{2H} = 0.5589$ (s) $+ 0.8293$ (p)	2.202	$S_{2H} = 0.7463$
C_5—H	$\psi_{5H} = 0.4815$ (s) $+ 0.8765$ (p)	3.314	$S_{5H} = 0.6986$
1,4-Cyclohexadiene			
C_1—C_2	$\psi_{12} = 0.6083$ (s) $+ 0.7937$ (p)	1.702	$S_{12} = 0.7663$
	$\psi_{21} = \psi_{12}$		
C_2—C_3	$\psi_{23} = 0.5555$ (s) $+ 0.8315$ (p)	2.241	$S_{23} = 0.6857$
	$\psi_{32} = 0.5119$ (s) $+ 0.8590$ (p)	2.816	
C_1—H	$\psi_{1H} = 0.5669$ (s) $+ 0.8238$ (p)	2.112	$S_{1H} = 0.7347$
C_3—H	$\psi_{3H} = 0.4878$ (s) $+ 0.8730$ (p)	3.203	$S_{3H} = 0.7105$

method are consistent with the above structural data. When hybrids are optimized for the nonplanar molecule the deviation angle $\delta = 0$ is obtained, *i. e.* no bending of bonds. This should be compared with the value $\delta = -1.25^0$ which results for a planar model. The deviation angle δ found for planar 1,3-cyclohexadiene is small compared with deviation angles in 1,3,5-cyclo-heptatriene ($\delta = -4^0$), and 1,3,5,7-cyclooctatetraene ($\delta = -7.5^0$), which is in accordance with the lesser degree of the nonplanarity for the former molecule.

The methylene C—H hybrids have unexpectedly large p-content ($sp^{3.31}$), the consequence of which is a small H—C—H angle (approx. 107.5^0). This is not in complete agreement with the experimentally observed value of 99^0, but definitely indicates that the unusually small angle is structural characteristics of methylene group in such an environment. It is a consequence of the presence of short carbon—carbon single bonds: 1.494 Å and 1.510 Å for C_4—C_5 and C_5—C_6 distances respectively, which favour larger participation of s-orbitals in C—C bonds. The corresponding C—C bond overlaps are considerably larger ($S_{56} = 0.6733$ and $S_{45} = 0.6839$) than are the usual values (~ 0.65).

Finally a related molecule 1,4-cyclohexadiene is considered, for which the electron diffraction measurements suggest that the planar conformation is by far the most probable, but the possibility that other, nearly planar conformations are present cannot be discarded with certainty[10]. The hybrids and the bond overlaps obtained for a planar structure (Table II) are similar to the corresponding results for 1,3-cyclohexadiene. In particular the methylene C—H hybrids are rich in p-character and again are associated with a small H—C—H angle. The deviation angle $\delta = -1.25^0$ suggests that a slight bending of the skeleton might be possible, and from the comparison with 1,3-cyclohexadiene one may expect that the angle characterising a nonplanarity will be similar in both molecules.

We may say in conclusion that the criterion of maximum overlap gives us an additional insight into the origin of the nonplanarity of the molecules considered. However, it is difficult to estimate the relative role of hybridization and delocalization of π-electrons in these molecules. For instance, it is difficult to understand the origin of the observed C—C bond shortenings, in fact the both factors contribute to bond character. It is not simple to estimate the partial contribution to the energy balance of the two opposing effects: π-overlapping and the deviation of σ-bonds from the molecular C—C skeleton, which are the largest for planar structures, and which come into a balance for the particular nonplanar conformations. Other factors also play some role, and the energy balance is very delicate. For example, 1,3,5,7-cyclooctatetraene is nonplanar, but one or two additional electrons in the π-system of the molecule would convert it into a planar form, although the contribution of those electrons to the π-electron energy is *zero* in the Hückel approximation.

REFERENCES

1. M. T r a e t t e n b e r g, *J. Am. Chem. Soc.* **86** (1964) 4265.
2. S. S. B u t c h e r, *J. Chem. Phys.* **42** (1965) 1833.
3. E. W. A b e l, M. A. B e n n e t t, and G. W i l k i n s o n, *Proc. Chem. Soc.* **1958**, 152.
4. M. R a n d i ć and Z. M a k s i ć, *Theoret. Chim. Acta* **3** (1965) 59.
5. L. K l a s i n c, Z. M a k s i ć, and M. R a n d i ć, *J. Chem. Soc.* **1966** (A) 755. *of Research and Development* **9** (1965) 2.
6. E. C l e m e n t i, *Tables of Atomic Functions,* a supplement to: IBM *Journal of Research and Development* **9** (1965) 2.
7. L. K l a s i n c, D. S c h u l t e - F r o h l i n d e, and M. R a n d i ć, *Croat. Chem. Acta* **39** (1967) 125.
8. O. B a s t i a n s e n, K. H e d b e r g, and L. H e d b e r g, *J. Chem. Phys.* **27** (1957) 1311.

9. G. Dallinga, and L. H. Toneman, *J. Mol. Structure* 1 (1967—68) 11.
10. G. Dallinga and L. H. Toneman, *J. Mol. Structure* 1 (1967—68) 117.
11. S. S. Butcher, *J. Chem. Phys.* 42 (1965) 1830.
12. G. Luss and M. D. Harmony, *J. Chem. Phys* 43 (1965) 3768.

IZVOD

Hibridizacija 1,3,5-cikloheptatriena i nekih srodnih molekula metodom maksimalnog prekrivanja

Z. Meić i M. Randić

Metodom maksimalnog prekrivanja izračunata je hibridizacija 1,3,5-ciklohepta-triena, 1,3,5,7-ciklooktatetraena, 1,3-cikloheksadiena i 1,4-cikloheksadiena. Ako za gornje molekule pretpostavimo planarnu strukturu, rezultati pokazuju odstupanja hibrida koji opisuju C—C veze kostura molekula od spojnica susjednih atoma. Devijacija iznosi od 1.25^0 do 7.5^0, a hibridi su usmjereni prema unutrašnjosti prstena molekule. Za neplanarne strukture, koje se osnivaju na eksperimentalnim podacima, kut devijacije se smanjuje ili je jednak nuli. Dakle, poprimanjem neplanarne geome-trije ove molekule reduciraju napetost koju bi inače planarnost ovih molekula zahti-jevala. Tako su ovi rezultati u skladu s eksperimentalnim rezultatima.

INSTITUT »RUĐER BOŠKOVIĆ«
ZAGREB