

Maximum Overlap Molecular Orbitals in Square Pyramidal $(\text{CH})_5^+$ Cation

King-Mo Sun and Wai-Kee Li*

Department of Chemistry, The Chinese University of Hong Kong, Shatin,
N. T., Hong Kong

Received March 11, 1976

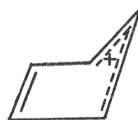
Applying the maximum overlap criterion, the localized molecular orbitals of square pyramidal $(\text{CH})_5^+$ cation have been determined. The resulting multi-center bonding orbitals are examined in detail. In addition, the basal C—C and all C—H bonds are compared with those of the more familiar systems, *e. g.*, cyclobutane and cyclobutene.

INTRODUCTION

Based on their extended Hückel calculations, Stohrer and Hoffmann¹ have suggested that the *unique* stable structure for the $(\text{CH})_5^+$ cation is a square pyramid (*1*, C_{4v} symmetry). This intriguing suggestion has generated a lot of experimental interest². In particular, a disubstituted *1* with a methyl group at the apex and at one basal carbon has been synthesized and characterized³.



1



2

On the theoretical side, modified CNDO⁴, MINDO/3⁵, and *ab initio*⁶ calculations all agree that *1* is a minimum on the $(\text{CH})_5^+$ energy surface. In addition, both CNDO and MINDO/3 calculations indicate the existence of another minimum: *2* (C_s symmetry). These two models disagree, however, as to which form is of lower energy.

Between species *1* and *2*, *1* appears to hold greater structural interest: it has a five-coordinated carbon atom and it is essentially isoelectronic with pentaborane(9). Therefore, it is desirable to study this system further with the maximum overlap model, which has been proven to be quite successful with hydrocarbon compounds⁷.

Besides being interesting structurally, the electron-deficient $(\text{CH})_5^+$ cation also provides a good test for the maximum overlap model. Up to now, the only systems, where multi-center bonding is involved, having been treated

* Address correspondence to this author.

by this model are the rather simple cases of CH_5^+ and diborane⁸. In these two cases, the atomic orbitals of the ligand, hydrogen, is known and the direct boron-boron overlap in B_2H_6 may be neglected. However, in the more general hydrocarbon systems, the overlaps between carbon atoms have to be taken into account and the hybrids used in the formation of the carbon-carbons are to be determined.

METHOD OF CALCULATION AND RESULTS

In a review paper⁹, Löwdin has pointed out that the magnitude of the smallest eigenvalue of the overlap matrix is a measure of the near linear dependence of the basis set. Looking at this argument from the opposite viewpoint, Lykos and Schmeising¹⁰ have suggested that the largest eigenvalue of the overlap matrix should be a measure of maximum overlap. They then proceed to prove analytically that the eigenvectors of the overlap matrix, ordered according to the eigenvalues to which they belong, represent a set of orthogonal molecular orbitals satisfying the criterion of the maximum overlap.

The maximum overlap molecular orbitals so obtained are, of course, delocalized in nature. By suitable linear combination of these orbitals, localized orbitals can be obtained. Indeed, for AX_n -type molecules, Lykos and Schmeising have shown explicitly how to construct the localized orbitals. For the system under investigation, the procedure has to be modified slightly. However, the underlying principle is essentially the same.

In applying the procedure of Lykos and Schmeising to 1, the structural data as reported by Dewar and Haddon⁵ have been assumed. (These data were obtained by full optimization of all the structural parameters.) The orientation of coordinates and the numbering of atoms are shown in Figure 1. The atomic wave functions used in the calculation of two-center overlaps are the familiar Clementi orbitals¹¹.

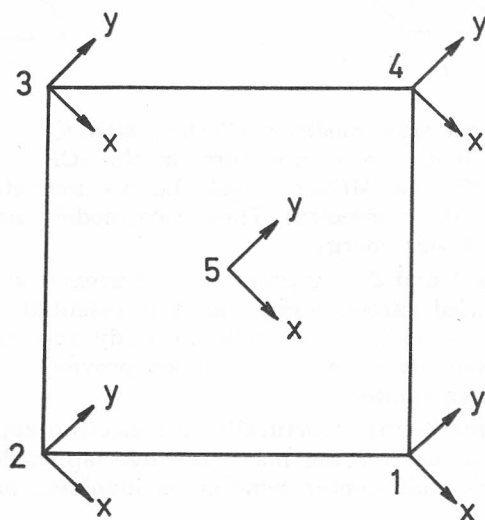


Figure 1. The numbering and coordinate systems in pyramidal $(\text{CH})_5^+$ cation.

By symmetry arguments, the basis set upon which the hybrid set is constructed consists of four A_1 orbitals, one B_1 orbital, one B_2 orbital, and three doubly degenerate E orbitals. These maximum overlap molecular orbitals can be linearly combined to form the localized ones. Only the localized orbitals are reported here; they are given in Table I. For further details, the following data are available from the last-named author: (i) the overlap matrix, (ii) the eigenvectors (with eigenvalues greater than 1) of the overlap matrix, and (iii) the matrix transforming the delocalized orbitals into localized ones. In addition, it is noted that, in the construction of the overlap matrix, only the following types are included: all carbon-carbon and C_i-H_i overlaps. In other words, all C_i-H_j and H_i-H_j overlaps have been ignored due to their anticipated smallness.

DISCUSSION

From Table I, it is seen that the bonding orbitals in I may be described as follows: Φ_1 to Φ_5 are the C_1-H_1 to C_5-H_5 bonds respectively; Φ_6 to Φ_9 are the C_1-C_2 , C_2-C_3 , C_3-C_4 , and C_4-C_1 bonds respectively; Φ_{10} and Φ_{11} are three-center bonds covering $C_1-C_5-C_3$ and $C_2-C_5-C_4$ respectively; Φ_{12} is a five-center bond encompassing all five carbon atoms.

The multi-center bonds are examined first. Orbitals Φ_{11} and Φ_{12} are shown schematically in Figures 2 and 3 respectively. The atomic orbitals forming the three-center bonds (Φ_{10} and Φ_{11}) are nearly pure p orbitals, p_z orbitals for the basal carbons and p_x or p_y for the apical carbon. The orbitals of the basal carbons deviate 5.2° from their respective z -axes, toward the apical carbon atom (Figure 2). Compared to the orbitals used in the three-center bonds, the basal atomic orbitals used in the five-center bond have higher s -character; these orbitals make an angle of 12.1° with their respective z -axes (Figure 3). This angle is considerably larger than those in the three-center bonds. This can readily be understood by noting that the orbitals of the apical carbon used in the three-center bonds, *i. e.*, p_x or p_y , point in such a direction that significant overlap can be resulted by a slight deviation of the basal carbon orbitals from z -axes. On the other hand, the apical carbon hybrid participating in the

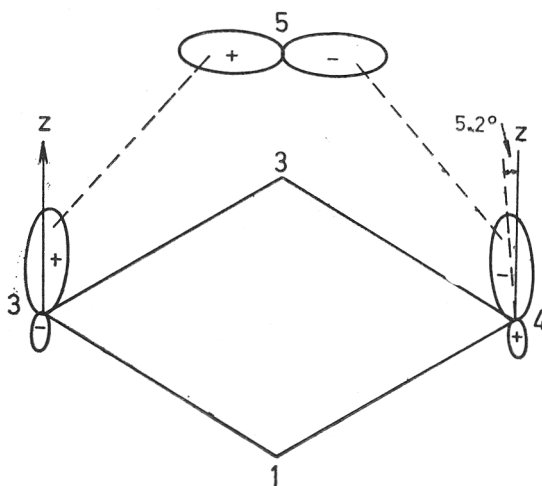


Figure 2. A schematic diagram of the three-center bond Φ_{11} .

TABLE I
Localized Orbitals of Square Pyramidal $(CH)_5^+$ Cation

A.		M. O.											
O.	Φ_1	Φ_2	Φ_3	Φ_4	Φ_5	Φ_6	Φ_7	Φ_8	Φ_9	Φ_{10}	Φ_{11}	Φ_{12}	
C ₁	s	.4186	.0012	.0311	.0012	.0031	.3137	.0026	.0026	.3137	.0362	.1379	
	p _x	.5343	-.0021	-.0075	-.0021	-.0542	-.1855	-.0104	-.0104	-.1855	.0490	-.0823	
	p _y	.0001	.0256	-.0001	-.0256	.0000	.5285	.0284	.0284	.5285	.0000	.0000	
C ₂	p _z	-.0254	-.0276	-.0296	-.0276	-.1347	-.2369	.0455	.0455	-.2369	.5425	.3864	
	s	.0012	.4186	.0012	.0311	-.0031	.3137	.0026	.0026	.3137	.0362	.1379	
	p _x	-.0256	.0001	.0256	-.0001	.0000	.5285	.0284	.0284	-.0627	.0000	.0000	
C ₃	p _y	.0021	-.5343	.0021	-.0075	.0542	-.1855	.0104	.0104	.0001	.0490	.0823	
	p _z	-.0276	-.0254	-.0296	-.0276	-.1347	-.2369	.0455	.0455	.0002	.5425	.3864	
	s	.0311	.0012	.4186	.0012	-.0031	.0026	.3137	.0026	-.0362	.0000	.1379	
C ₄	p _x	.0075	.0021	-.5343	.0021	.0542	.0104	.1855	.0104	.0490	.0001	.0823	
	p _y	.0001	.0256	-.0001	-.0256	.0000	.5285	.0284	.0284	.0000	.0627	.0000	
	p _z	-.0296	-.0276	-.0254	-.0276	-.1347	-.2369	.0455	.0455	-.5425	.0002	.3864	
C ₅	s	.0012	.0311	.0012	.4186	-.0031	.0026	.0026	.0026	.3137	.0362	.1379	
	p _x	-.0256	.0001	.0256	-.0001	.0000	.5285	.0284	.0284	-.0627	.0000	.0000	
	p _y	-.0021	-.0075	-.0021	-.5343	.0542	-.1855	-.0104	-.0104	.0001	.0490	.0823	
C ₅	p _z	-.0276	-.0296	-.0276	-.0254	-.1347	.0455	.0455	.0455	-.5425	.0002	.3864	
	s	.0012	.0012	.0012	.0012	.3196	.0384	.0384	.0384	.0000	.0000	.5059	
	p _x	-.0099	.0002	.0099	-.0002	.0000	.0356	.0356	.0356	.6463	.0003	.0000	
H ₁	p _y	.0002	.0099	-.0002	.0099	.0000	.0354	.0354	.0354	.0000	.6463	.0000	
	p _z	.0453	.0453	.0453	.0453	.5041	.0158	.0158	.0158	.0000	.0000	-.0169	
	1s	7283	-.0032	.0155	-.0032	-.0520	.0342	.0342	.0342	.0361	.0001	.0255	
H ₂	1s	-.0032	.7283	-.0032	.0155	-.0520	.0275	.0275	.0275	.0001	.0361	.0255	
	1s	-.0155	-.0032	.7283	-.0032	-.0520	.0342	.0342	.0342	.0361	.0001	.0255	
	1s	-.0032	-.0155	-.0032	.7283	-.0520	.0342	.0342	.0342	.0001	.0361	.0255	
H ₃	1s	-.0032	.0319	-.0032	.0319	.6855	-.0524	-.0524	-.0524	.0000	.0000	.0199	
	1s	.0319	-.0032	.0319	-.0032	.6855	-.0524	-.0524	-.0524	.0000	.0000	.0199	
	1s	.0319	.0319	.0319	.0319	.6855	-.0524	-.0524	-.0524	.0000	.0000	.0199	

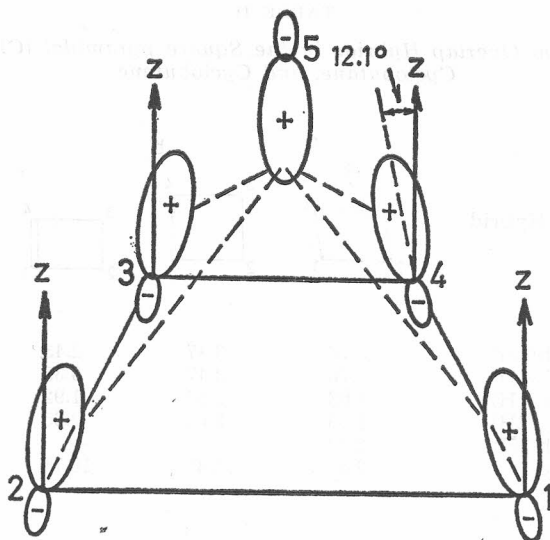


Figure 3. A schematic diagram of the five-center bond Φ_{12} .

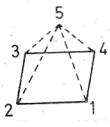
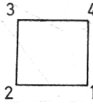

five-center bond, which consists mostly of s orbital with slight mixing from the p_z orbital, points directly downward. Therefore, to result in a more effective overlap, the basal carbon orbitals have to have a larger deviation from the z-axes. Another reason may be that, with higher p-character, the basal carbon orbitals forming the three-center bonds can extend farther than those in the five-center bond do, which again would lead to smaller deviation angles. The result that the hybrid of the apical carbon used in forming the five-center bond has exceptionally high s-character is due to the difference between the following two overlap integrals: $(2s_C, 2p_C; 1.583 \text{ \AA}) = 0.40426$, $(2p_C, 2p_C; 1.583 \text{ \AA})_z = 0.26848$, where 1.583 \AA is the distance between the apical and basal carbons⁵. As a consequence of this, the carbon hybrid used in the formation of $\text{C}_5 - \text{H}_5$ bond has rather high p-character, with hybridization index n being 2.49. [Hybridization index of a hybrid is defined as the ratio of its p- and s- populations.]

In tilting the basal carbon orbitals to ensure effective overlap in the multi-center bonds, the basal hydrogens are directed upward from the base of the square pyramid, as in the case of pentaborane(9). By the same reasoning, the carbon hybrids forming the base of the square pyramid are directed downward. In fact, the deviation angles, which are about 30° , are not common in a four-membered ring.

For the sake of comparison, the maximum overlap hybrids in cyclobutane¹², cyclobutene, and 1 are summarized in Table II. It can be readily seen that, in 1, there are approximately two p orbitals taking part in the hybridization of a basal carbon atom to form the localized C—H and C—C bonds. So, it is expected that the basal carbon should have similar hybridization to that of C_1 in cyclobutene. It can be seen from Table II that this is true for the C—H hybrids. But the index n of the hybrids forming the base of the square pyramid of $(\text{CH})_5^+$ is similar to the hybrids forming the C—C bonds of cyclobutane.

TABLE II

The Maximum Overlap Hybrids in the Square pyramidal $(CH)_5^+$ Cation, Cyclobutane, and Cyclobutene

Hybrid	a	b	c
			
$h(12)^d$	3.76	3.47	2.43
$h(21)$	3.76	3.47	3.35
$h(1H)^d$	1.63	2.62	1.92
$h(2H)$	1.63	2.62	2.65
$h(5H)$	2.49	—	—
d_{12}^e	33.5°	8.4°	10.7°

^a From Table I.

^b Ref. 12.

^c Ref. 7.

^d Hybrid orbital $h(ij)$ is directed from C_i to C_j ; hybrid $h(iH)$ points from C_i to the hydrogen atom linking with C_i . Each numerical value given in this Table is the hybridization index n in the hybrid sp^n .

^e Deviation angle d_{ij} is the angle between bond C_i-C_j and the hybrid $h(ij)$.

This may be due to the extraordinary large deviation angle. (A large deviation angle for a hybrid inevitably leads to high p -character.) Furthermore, part of the s orbital of the basal carbon atom is consumed in the formation of the five-center bond. Since $C-H$ bonds are always assumed to be straight, no deviation angle is involved and the hybridization is as expected.

From above discussion, it appears that a concise model describing the bonding of the square pyramidal structure of $(CH)_5^+$ may be obtained by applying the maximum overlap criterion. The results are summarized as follows:

(i) The apical carbon atom is bonded to the other four carbon atoms by a five-center bond and two three-center bonds.

(ii) The hybrids forming the base of the square pyramid are similar to those of cyclobutane but with exceptionally large deviation angles.

(iii) The basal $C-H$ bonds are similar to C_1-H of cyclobutene.

(iv) The apical $C-H$ bond has rather high p -character, hybridization index for the carbon hybrid participating in this bond being about 2.50.

Acknowledgment. The authors wish to thank Professors M. Randić and Z. B. Maksić for their helpful correspondences.

REFERENCES

1. W.-D. Stohrer and R. Hoffmann, *J. Amer. Chem. Soc.* **94** (1972) 1661.
2. See, for example, H. Hart and M. Kuzuya, *J. Amer. Chem. Soc.* **94** (1975) 2450 and references cited therein.
3. S. Masamune, M. Sakai, H. Ona, and A. J. Jones, *J. Amer. Chem. Soc.* **94** (1972) 8956.
4. H. Kollmar, H. O. Smith, and P. v. R. Schleyer, *J. Amer. Chem. Soc.* **95** (1973) 5834.

5. M. J. S. Dewar and R. C. Haddon, *J. Amer. Chem. Soc.* **95** (1973) 5836.
6. W. J. Hehre and P. v. R. Schleyer, *J. Amer. Chem. Soc.* **95** (1973) 5837.
7. M. Randić and Z. B. Maksić, *Chem. Rev.* **72** (1972) 43.
8. Z. B. Maksić and M. Randić, *J. Mol. Structure* **6** (1970) 215.
9. P.-O. Löwdin, *Ann. Rev. Phys. Chem.* **11** (1960) 107.
10. P. G. Lykos and H. M. Schmeising, *J. Chem. Phys.* **35** (1961) 288.
11. E. Clementi, a supplement to IBM. *J. Res. Develop.* **9** (1965) 2.
12. L. Klasinc, Z. Maksić, and M. Randić, *J. Chem. Soc. A* (1966) 755.

SAŽETAK

Molekularne orbitale maksimalnog prekrivanja za $(\text{CH})_5^+$ kation konfiguracije kvadratne piramide

K. M. Sun i W. K. Li

Izračunane su molekularne orbitale maksimalnog prekrivanja za kation $(\text{CH})_5^+$ konfiguracije kvadratne piramide. Dobivene molekularne orbitale lokalizirane su, a parametri hibridizacije za CC- i CH-veze uspoređeni su s odgovarajućim vrijednostima za ciklobutan i ciklobuten. Pokazano je da hibridi CH-veze osnove imaju mnogo veći s-karakter od CH-veza na vrhu piramide.

DEPARTMENT OF CHEMISTRY
THE CHINESE UNIVERSITY OF HONG KONG
SHATIN
N. T. HONG KONG

Prispjelo 11. ožujka 1976.