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## Structure and Charge Distribution of the (CH)<sub>62</sub>+ Dication

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STRUCTURE AND CHARGE DISTRIBUTION OF THE  $(\text{CH})_6^{2+}$  DICATION

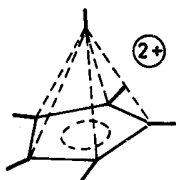
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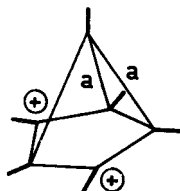
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In a preceding paper Hogeveen and Kwant<sup>1</sup> report PMR and CMR measurements on the species  $(\text{C-CH}_3)_6^{2+}$ . The authors conclude that the most likely structure of this dication is a nonclassical one of approximate symmetry  $C_{5v}$  (fig. 1a) although classical structures of lower symmetry (fig. 1b) cannot be completely excluded.



1a



1b

It seemed of interest therefore to carry out some exploratory ab initio molecular orbital calculations in order to investigate the feasibility of symmetrical structures of the kind proposed and their stability with respect to less symmetrical alternatives.

Conventional closed shell SCF-MO calculations<sup>2</sup> on the minimal basis-3GTO - level have been carried out for the simpler species  $(\text{CH})_6^{2+}$  in two sets. In the first set the geometry was constrained to  $C_{5v}$  symmetry and optimal values were determined for the C-C distance (R) in the ring and the position (h) of the CH group above the ring. All CH distances were kept fixed at 1.10 Å.

In the second set of calculations the symmetry was relaxed to  $C_s$  by moving the CH group above the ring off the  $C_5$  axis in a plane of symmetry, in combination with various deformations of the ring. For the computations of the first set the program POLYATOM<sup>3</sup> as well as the much faster program GAUSS 70<sup>4</sup> were employed. Most of the calculations of the second set were done with GAUSS 70 only. In both programs a contracted basis set of 3 GTO's per atomic orbital was used. In the POLYATOM calculations contraction coefficients and exponents were chosen that minimized the ground state energies of the atoms C and H<sup>5</sup>. In the GAUSS 70 runs the standard minimal basis set of the program was employed. For comparison purposes similar calculations were made on the ions  $(CH)_5^+$  and  $(CH)_5^-$ . In Table I optimal values for R and L, corresponding total energies and various Mulliken gross charges are listed which resulted from the GAUSS 70 calculations.

	R(Å)	h(Å)	E <sub>total</sub> (A.U.)	C <sub>1</sub> <sup>a</sup>	H <sub>1</sub> <sup>a</sup>	C <sub>6</sub> <sup>b</sup>	H <sub>6</sub> <sup>b</sup>	ring <sup>c</sup>
$(CH)_5^-$	1.39		-189.730	-0.16	-0.04			-1.00
$(CH)_5^+$	1.43		-189.558	0.04	0.16			1.00
$(CH)_6^{2+}$	1.45	1.21	-227.124	0.08	0.26	0.00	0.28	1.71

Table I. Optimal distances, total energies and gross charges.

a. ring atoms, b. top atoms, c. total charge on ring.

The POLYATOM results yielded lower total energies (-227.803 A.U. for the dication) as expected but much larger equilibrium distances ( $R=1.53$  Å,  $h=1.38$  Å). Table II displays the behavior of the energy as a function of h with R fixed at 1.45 Å. Except for the shift in equilibrium distances the POLYATOM calculations give nearly the same results.

h (Å)	1.17	1.20	1.21	1.22	1.27	1.30	1.40	1.50
E (kcal/mol)	1.16	0.063	0.000	0.056	1.8	4.4	19.0	41.4

Table II. Energy differences with respect to equilibrium conformation.

The second set of computations consisted of many runs based on structure 1b. As yet no evidence was found of other stable nonplanar conformations. The lowest energies obtained were still about 25 kcal/mol higher than the energy of the symmetrical structure.

In the structures considered no low-lying unoccupied orbitals are available to construct excited configurations that could interact significantly with the Hartree-Fock ground state. Therefore this level of approximation should be adequate to discuss at least the gross features of the minimum energy surface. Furthermore, experience has shown that the particular minimum basis set chosen in GAUSS 70 yields geometries for hydrocarbons that compare well with experimental data. Considering these facts we feel that our results strongly support the symmetrical structure for  $(C-CH_3)_6^{2+}$  proposed. Our calculations not only show a remarkable stability for this structure compared to less symmetrical structures, but also they yield effective charges on the  $C_5$  ring and on the top C atom that are quite consistent with the experimental findings. Details of the bonding can be derived from the overlap populations between the  $\sigma$  and  $\pi$  orbitals of the top CH group and those of the ring which are listed in Table III.

CH	ring	$\pi$	$\sigma$	total
$\pi$		0.453	-0.013	0.440
$\sigma$		0.250	-0.092	0.158
total		0.703	-0.105	0.598

Table III. Overlap populations between CH and the ring.

For the ring the  $\pi$  orbitals are determining for the bonding as expected. For the CH group each of the  $\sigma$  and  $\pi$  orbitals is of about equal importance. The total overlap population of 0.598 is indicative of the strong bonding when it is compared with the total overlap population between two nearest neighbour C atoms in the ring of 0.412 (0.50 in  $(CH)_5^+$ ). Finally the gross atomic orbital

populations obtained for the top CH group,  $\sigma_{\text{CH}}^2 \pi)^{1.76} \sigma)^{0.96}$ , may be used to visualize the type of bonding in a way closely related to that in transition metal coordination compounds. Starting from a  $(\text{CH})^+$  valence configuration of  $\sigma_{\text{CH}}^2 \pi)^2 \sigma)^0$  one might say that 0.96 electrons have been donated to the empty  $\sigma$  orbital of  $(\text{CH})^+$  accompanied by a  $\pi$ -backdonation of 0.24 electrons to the  $(\text{CH})_5^+$  ring.

#### References

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