1. Jensen, K. A. and Nielsen, P. H. *Acta Chem. Scand.* **17** (1963) 547, 549.
2. Jensen, K. A., Carlsen, J. B., Holm, A. and Nielsen, P. H. *Acta Chem. Scand.* **17** (1963) 550.
3. Jensen, K. A. and Henriksen, L. *Acta Chem. Scand.* **22** (1968) 1107.
4. Anthoni, U., Dahl, B. M., Larsen, Ch. and Nielsen, P. H. *Acta Chem. Scand.* **23** (1969) 1061.
5. Jensen, K. A. and Anthoni, U. *Acta Chem. Scand.* **24** (1970). *In press.*
6. Jensen, K. A. and Henriksen, L. *Acta Chem. Scand.* **24** (1970). *In press.*
7. Jensen, K. A. and Krishnan, V. *Acta Chem. Scand.* **24** (1970) 1088.
8. Jensen, K. A. and Mygind, H. *Acta Chem. Scand.* To be published.
9. Ferrari, A., Braibanti, A., Bigliardi, G. and Lanfredi, A. M. *Acta Cryst.* **19** (1965) 548.
10. Braibanti, A., Lanfredi, A. M., Tiripicchio, A. and Loqiudice, F. *Acta Cryst.* **B 25** (1969) 93.
11. Castelli, A., Palm, A. and Alexander, Jr., C. *J. Chem. Phys.* **44** (1966) 1577.
12. Snyder, R. G. and Schachtschneider, J. H. *Spectrochim. Acta* **21** (1965) 169.
13. Müller, A. and Fadini, A. *Z. physik. Chem. Neue Folge* **54** (1967) 129.
14. Mecke, R. and Spiesecke, H. *Chem. Ber.* **89** (1956) 1110.
15. Anthoni, U. *Acta Chem. Scand.* **20** (1966) 2742.
16. Wilson, T. P. *J. Chem. Phys.* **11** (1943) 361.

Received April 10, 1970.

The Valence Electron Density Distribution of Strained Single Bonds in the Iterative Extended Hückel Approach

III. Pentacyclo[4.2.0.0²,⁵.0³,⁸.0⁴,⁷]octane (Cubane)*

OLLE MÅRTENSSON

Quantum Chemistry Group, Uppsala University, Box 518, S-751 20 Uppsala, Sweden

With cubanes we mean organic or inorganic compounds, the basic valence structure of which is cubic (Fig. 1; for a review see Ref. 1). Within organic chemistry the name cubane is used as a trivial name for pentacyclo[4,2,0,0²,⁵,0⁵,⁸0⁴,⁷]octane, C_8H_8, the parent hydrocarbon in its
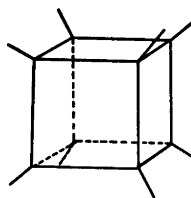

Fig. 1. The valence skeleton of cubanes.

class of compounds. The classical valence angle of the cubic structure, 90°, is the limiting angle for orthogonal hybrids built up from atomic orbitals of s and p type directed along the interatomic vectors. Complex hybrids may also be used for this description.[2] Since the cubanes are strained compounds, with the valence angles differing substantially from the tetrahedral angle, it is not unreasonable to expect bent bonds, *i.e.* bonds with the electron density forming maxima outside the interatomic vectors. If a hybrid interpretation of such a bond is desired, "best" hybrid orbitals may be chosen as those providing the highest localization of the MO-LCAO over-
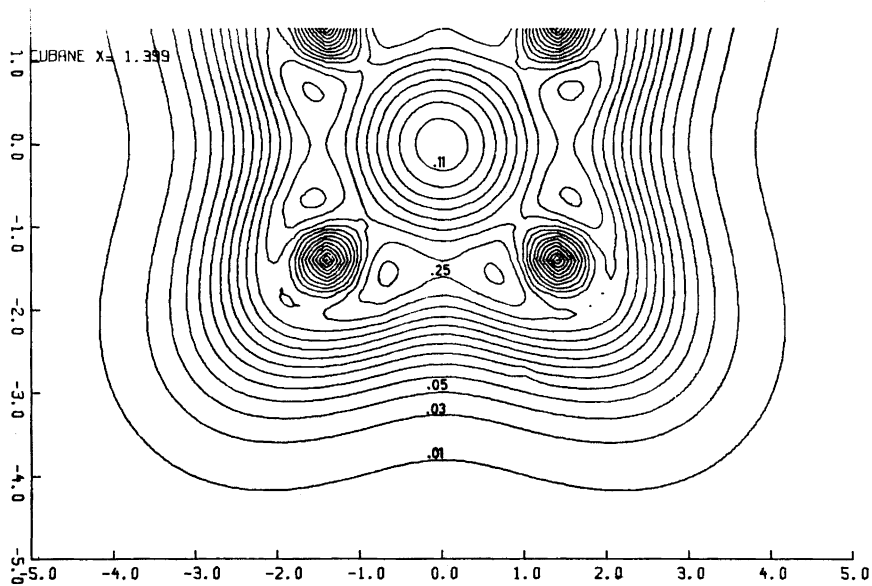
Fig. 2. Valence electron density distribution of cubane at the surface of the cube.
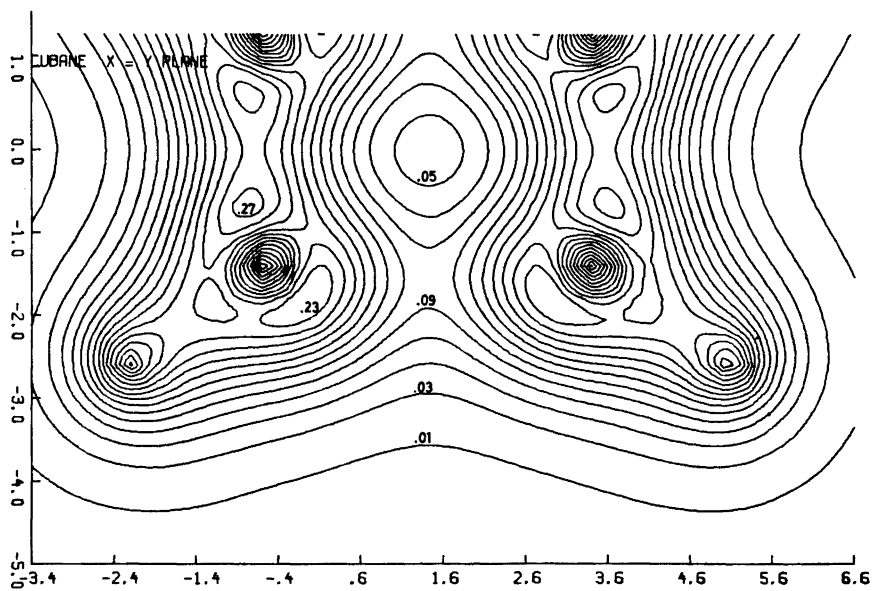

Fig. 3. Valence electron density distribution of cubane in the diagonal plane of the cube.

lap matrix as proposed by Del Re[3] and applied to cubane by Veillard and Del Re.[4] The hybridization in cubane in the method of maximum overlap has also been studied by Maksić et al.[5] The bent bond type of the C−C bonds can also be shown in a simple way by means of valence electron density level diagrams, since this density is a quantity closely related to the valence concept. We present here two diagrams, based on MO calculations, one showing the valence electron density distribution on the surface of the cube (Fig. 2) and the other in the diagonal plane of the cube (Fig. 3). The method for calculating the eigenvectors and the electron density and the plotting method have been reported earlier.[6] The geometry for cubane itself is now known from X-ray data.[1] The C−C distance is close to that of cyclobutane (1.548 Å). However, the eigenvectors used in the present calculation of the electron density are based on an interatomic distance of 1.48 Å applied in an earlier calculation. (Octaphenylcyclooctatetraene was originally and incorrectly ascribed a cubane structure.) For the present purpose, and with the present accuracy in plotting this difference in atomic distance is of little importance. The lack in full symmetry in

the level diagrams is also within the accuracy of plotting. The interatomic C−H distance used is 1.09 Å.

Fig. 2 shows that even in the surface plane of the cube the bent bond nature of the C−C bond can be observed. As expected the two density maxima are still more displaced from the interatomic line in the diagonal section of the cube (Fig. 3). The charge distribution resembles that of cyclopropane obtained by the same method.[6] In the center of the cube we have a minimum which is definitely lower than that at the center of the surface of the cube.

1. Tzschach, A. and Balzuweit, A. Z. Chemie 8 (1968) 121.
2. Mårtensson, O. and Öhrn, Y. Theoret. Chim. Acta (Berlin) 9 (1967) 133.
3. Del Re, G. Theoret. Chim. Acta (Berlin) 1 (1963) 197.
4. Veillard, A. and Del Re, G. Theoret. Chim. Acta (Berlin) 2 (1964) 55.
5. Maksić, Z., Klasinc, L. and Randić, M. Theoret. Chim. Acta (Berlin) 4 (1966) 273.
6. Mårtensson, O. and Sperber, G. Acta Chem. Scand. 24 (1970). In press.