

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

## II. Bicyclobutane\*

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The valence electron density in the IEH approach is given in the form of level diagrams for different sections of the bicyclobutane molecule. A pronounced concentration of electron density to the bridgehead carbon atoms is observed. This is of  $p$  type and thus differs from the density of an ordinary double bond with its delocalized  $\pi$  charge. A difference in the charge density of the two C—H bonds of the methylene groups can also be observed, the equatorial bond showing an increased charge density as compared to the axial bond which is almost unperturbed (as compared to a C—H bond of methane).

It is well known that so called strained single bonds are more reactive than ordinary single bonds and may show features which we generally consider typical for double bonds. Catalytic hydrogenation, addition of halogens, acids, and carbenes are examples of reactions characteristic for unsaturated bonds to which even strained single bonds may be more or less susceptible. UV spectra may also show the unsaturated nature of these strained bonds.

In this paper we will consider bicyclo[1.0.1.]butane and its bridgehead bond in particular, in which the strain so to speak is created by the combination of strains from two cyclopropane rings fused together in a common edge.

The density distribution is obtained from eigenvectors calculated in the IEH approach. This method and the technique for computing and plotting density level diagrams have been described earlier and will not be the subject of further comments here.<sup>1,2</sup>

The essential geometrical parameters of bicyclobutane, based on investigations of IR and Raman spectra, have been given by Haller and Srinivasan.<sup>3</sup> The molecule has  $C_{2v}$  symmetry (Fig. 1). Within the errors reported, the

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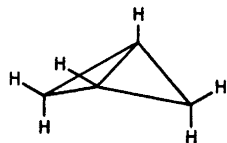


Fig. 1. The geometrical skeleton of bicyclo-[1.0.1.]butane.

molecule can be described as consisting of two equilateral triangular rings (C-C distance equal to 1.53 Å) which have been fused together in a common edge. The interplanar angle is  $126^\circ$  and the C-C-H angle of the bridgehead is  $163^\circ$ .  $120^\circ$  has been used for the H-C-H angle of the methylene groups and 1.09 Å for the interatomic C-H distance.

### RESULTS AND DISCUSSION

Fig. 2 displays the density distribution in the symmetry plane<sup>†</sup> which includes the bridgehead atoms. Pronounced density maxima above and below the centers of the bridgehead carbon atoms are seen. In order to check that they are not cylindrically symmetrical about the bridgehead line, we must

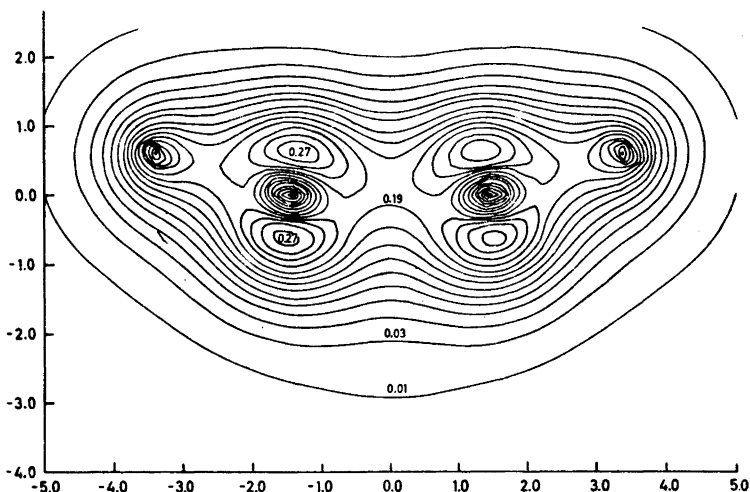


Fig. 2. Valence electron density of bicyclobutane in the section through the bridgehead carbon atoms and their hydrogen atoms.

consider a section through the center of the carbon atom perpendicular to the bridge line. From Fig. 3 we see that the maxima at the two bridgehead carbon atoms are of *p* type. The general picture is fairly similar to that of the C-C bond in cyclopropane (see Fig. 5 of Ref. 1), but the maxima at the bridgehead atoms of bicyclobutane are situated at almost right angles to the bridgehead line and are somewhat stronger.

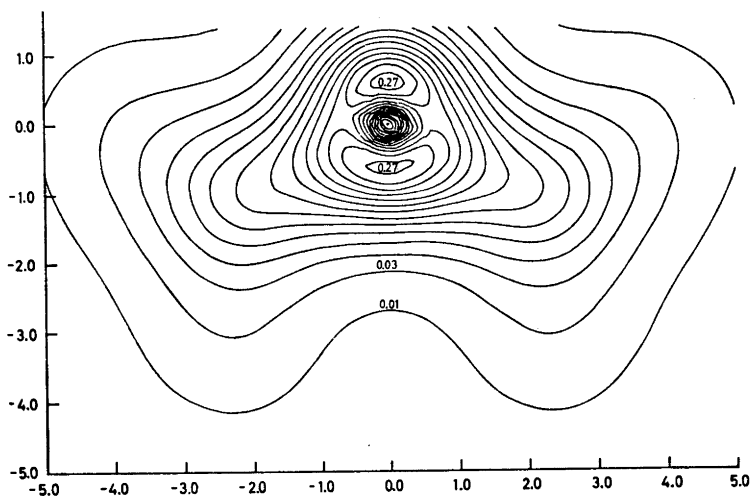


Fig. 3. Valence electron density of bicyclobutane in the section through a bridgehead carbon atom and perpendicular to the bridge.

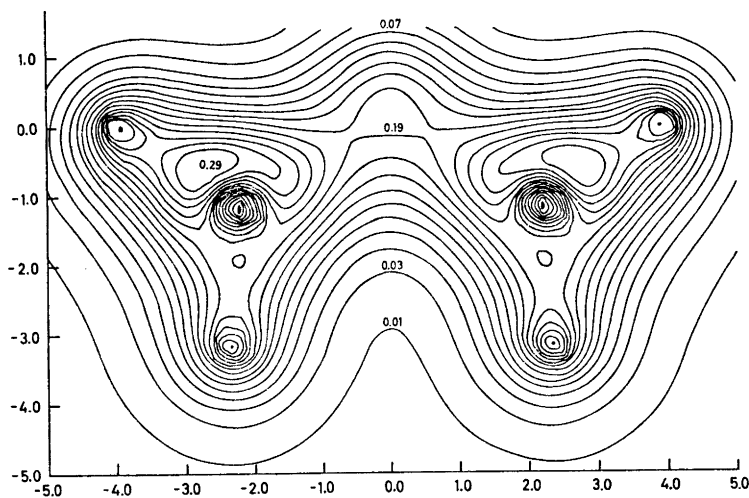


Fig. 4. Valence electron density of bicyclobutane in the symmetry plane, perpendicular to the bridge.

The density distribution in the other main symmetry plane (perpendicular to the bridgehead line and through the methylene groups) is given in Fig. 4. We see that the density distribution at the two C-H bonds of the methylene groups is different, that of the axial (or *endo*) one being somewhat perturbed

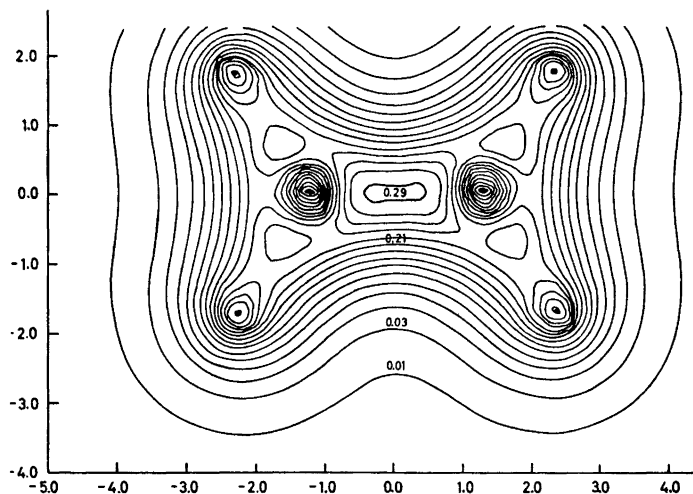


Fig. 5. Valence electron density ( $\sigma$  charge) of ethylene in the molecular plane.

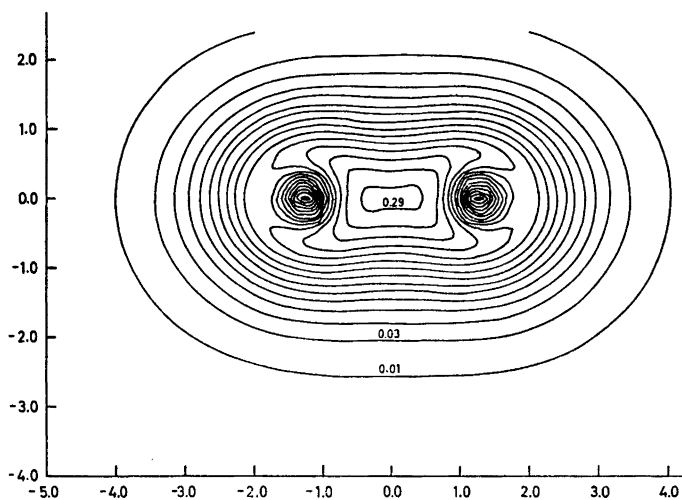


Fig. 6. Valence electron density of ethylene in the plane through the carbon atoms and perpendicular to the molecular plane.

(as compared to an ordinary C–H bond of, for instance, methane). The equatorial (or *exo*) C–H bond shows an obvious charge concentration of bent bond type towards the bridge, with its maximum displaced somewhat outside the interatomic C–H line. The maximum value is also higher than that of the interatomic maximum of an ordinary C–H bond. There are reasons to believe

that the different reactivity of these two positions in decarboxylation for instance may be correlated with a different picture in density distribution.

Since the bridgehead bond has properties which to some extent relates it to an ordinary double bond, it is of interest to compare it with such an unsaturated bond from the point of view of density distribution. Figs. 5–7 give the valence electron distribution in the three symmetry planes of ethylene. The distribution in the molecular plane as well as that in the plane perpendicular to it through the carbon atoms indicates the strong delocalization of the charge over the bond (see Figs. 5 and 6). But we must remember

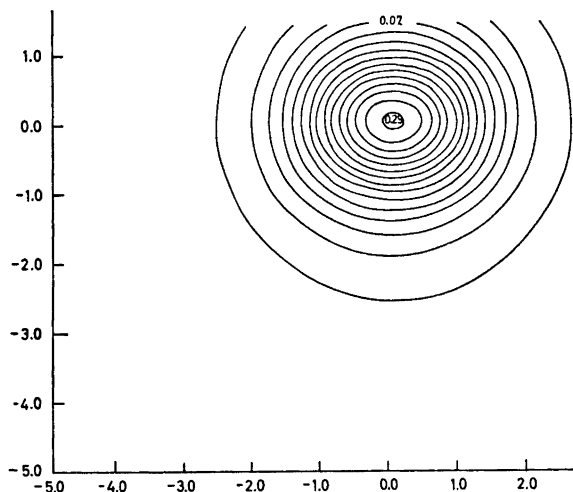


Fig. 7. Valence electron density in the plane perpendicular to the C–C interatomic vector and at its midpoint. The molecular plane of ethylene is vertical.

that we have two extra electrons which will create a higher electron density in the bond. In the strained bridge bond of bicyclobutane the maxima are created by rearrangement of the charge of the surrounding bonds. The similarity in chemical properties between a strained single bond and an ordinary double bond does not mean that the valence electron distribution is necessarily of the same type. Finally, Fig. 7 gives the density distribution in the symmetry plane perpendicular to the C–C interatomic axis. We see that the  $\sigma$  charge obviously predominates the picture, its circular symmetry being somewhat perturbed by the contributions from the  $\pi$  charge.

The chemical properties of bicyclobutane compounds have been thoroughly discussed by Pomerantz and Abrahamson.<sup>4</sup> They base their discussion on two molecular orbital models for the bicyclobutane skeleton constructed from carbon  $sp^2$  and  $sp$  hybrids, arranged intuitively to fit two types of overlap models. The triple overlap used in the construction of their model I is not in agreement with the density distribution of cyclopropane obtained in MO calculations including no hybrid consideration.<sup>2,5,6</sup> The second model, based

on an overlap maximum between the plane of the two rings, is certainly also different from that presented here, which will show a strong density difference maximum even outside the bridge bond.

Although valence electron density diagrams are very illustrative as giving an idea of the nature of the bonds and the shape of the molecule, it is perhaps too early to express any opinion about their value in discussions of reactivity. We must remember that the ground state properties of a molecule are not sufficient for understanding its chemical behaviour, and the level diagrams presented here refer, of course, only to the ground state.

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#### REFERENCES

1. Karlsson, G. and Mårtensson, O. *Theoret. Chim. Acta (Berl.)* **13** (1969) 195.
2. Mårtensson, O. and Sperber, G. *Acta Chem. Scand.* **24** (1970) 1749.
3. Haller, I. and Srinivasan, R. *J. Chem. Phys.* **41** (1964) 2745.
4. Pomerantz, M. and Abrahamson, E. W. *J. Am. Chem. Soc.* **88** (1966) 3970.
5. Kochanski, E. and Lehm, J. M. *Theoret. Chim. Acta (Berl.)* **14** (1969) 281.
6. Buenker, R. J. and Peyerimhoff, S. D. *J. Phys. Chem.* **73** (1969) 1299.

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