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## The Valence Electron Density Distribution of Strained Single Bonds in the Iterative Extended Hückel Approach. VI. The First Excited State Charge Density of Bicyclobutane \*

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The intention of this series of papers and related articles<sup>1,2</sup> has been to investigate to what extent the distribution of the valence charge can give information about the nature of strained single bonds and the interpretation of the valence concept in ground state molecules. Since fairly big molecules are treated, the iterative extended Hückel method was chosen. The results have been presented in the form of density level diagrams of pertinent sections of the molecules. In the case of strained single bonds, two maxima outside the classical valence line were obtained, a result which is in accordance with those obtained by more sophisticated methods

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on small molecules, for instance cyclopropane.<sup>3,4</sup> That this heaping up of charge outside the interatomic, straight line will be more pronounced when two or three cyclopropanes are "fused" together as in bicyclobutane and tricyclobutane, seems obvious. Chemically strained single bonds show some resemblance to the unsaturated bond, but this similarity is not reflected in the valence charge distributions, which are of quite different types in the two cases.

Although the IEH method is fairly naive, it has in calculations of this type the advantage of taking all overlap integrals between the valence orbitals under consideration. Therefore it might be of interest also to look at the first excited state densities. It should also be pointed out that the picture given of the first excited state charge density is a crude one also for the reason that excitation generally leads to deformation of the molecule and that calculations for molecules in excited states have to be based on another geometry than when the ground states are treated. To obtain easily interpreted density difference diagrams for semiquantitative considerations one prefers to have the same geometry.

The bridge bond of bicyclo[1.0.1.]butane was selected as an example of a strained single bond. The ground state charge density of this molecule has been treated by me some years ago,<sup>5</sup> but new structural data obtained from the microwave studies by Cox *et al.*<sup>7</sup> make a recalculation desirable. These data and others<sup>8</sup> indicate a considerably smaller value for the C-C-H bridgehead angle than that by Haller and Srinivasan<sup>9</sup> used by me earlier. These new calculations also incorporate the value of

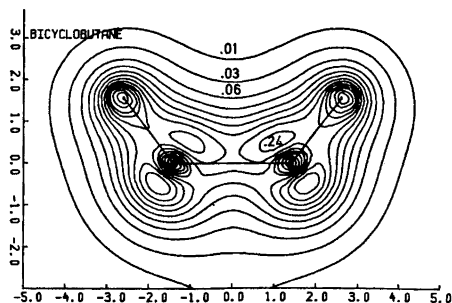


Fig. 1. Valence charge distribution of bicyclobutane in the symmetry plane through the bridgehead line. Ground state.

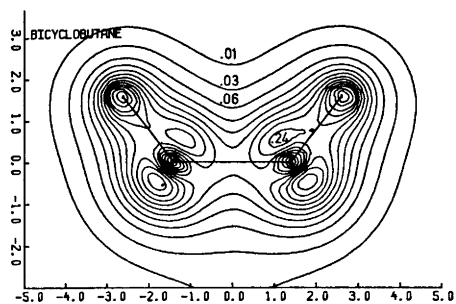


Fig. 2. Valence charge distribution of bicyclobutane in the symmetry plane through the bridgehead line, First excited state.

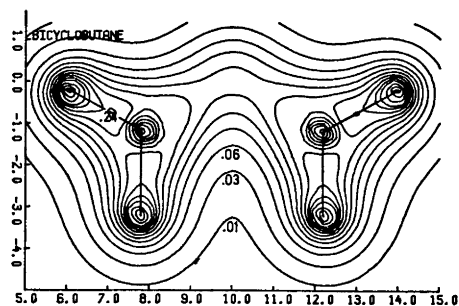


Fig. 5. Valence charge distribution of bicyclobutane in the symmetry plane perpendicular to the bridgehead line, First excited state.

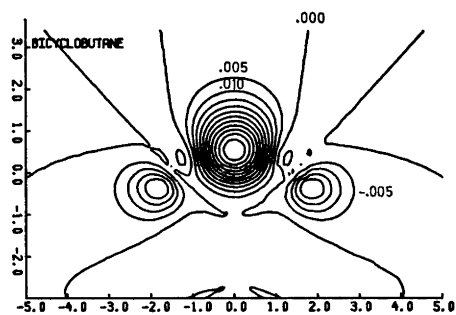


Fig. 3. Density difference between ground state (Fig. 1) and first excited state (Fig. 2) of bicyclobutane in the symmetry plane through the bridgehead line.

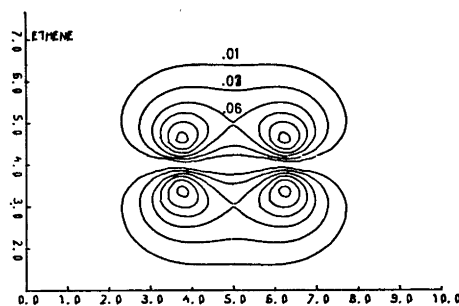


Fig. 6.  $\pi$  charge distribution of ethene in the symmetry plane perpendicular to the molecular plane, Ground state.

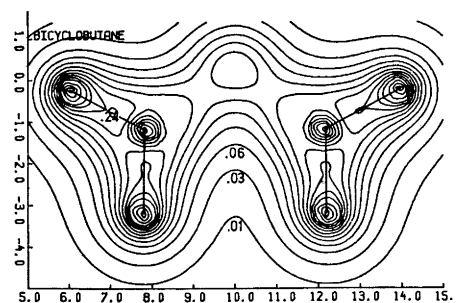


Fig. 4. Valence charge distribution of bicyclobutane in the symmetry plane perpendicular to the bridgehead line, Ground state.

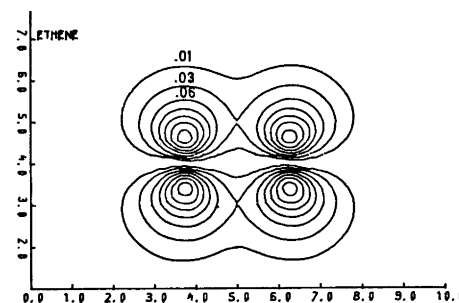


Fig. 7.  $\pi$  charge distribution of ethene in the symmetry plane perpendicular to the molecular plane, First excited state.

1.2 (instead of 1.0) for the orbital exponent of the Slater  $1s$  orbitals for hydrogen.<sup>8</sup> The calculation itself and the plotting procedure have been described previously.<sup>1</sup>

As regards the two ground state diagrams (Figs. 1 and 4 corresponding to Figs. 2 and 4 of Ref. 5), the decreased value of the bridgehead angle and the increased value of the hydrogen  $1s$  orbital exponent lead to a charge distribution with the outer maxima more displaced towards each other and the relationship with cyclopropane is obvious. A corresponding outward displacement of the interior maxima has also taken place. On the other hand the increased value of the exponent of the hydrogen  $1s$  functions is essentially responsible for a less pronounced difference in density between the equatorial and axial C-H bonds of the methylene groups than in the preceding calculations.

The corresponding diagrams of the first excited state density (Figs. 2 and 5) indicate a flow of charge from the space between the carbon atoms of the bridgeheads and the space in front of the bridgehead line. On the other hand there is an increase of charge in the interior maxima. These changes are in a simple way illustrated by means of the density difference between the ground state and the first excited state densities (Fig. 3).

Because of their reactivity strained single bonds are often compared with double bonds. Thus they have some character of "unsaturation". As regards the valence charge such a comparison is difficult to make. If we compare the bridgehead bond in bicyclobutane with the

C-C bond of ethene, we find that the first excited state transition in ethene is a  $\pi-\pi'$  transition with full retention of the charge symmetry about the classical valence line. The picture here is simple since we have a lower  $\pi$  charge density between the two carbon atoms in the first excited state (the  $\sigma$  charge is not changed), and this charge is more concentrated to the sites of the carbon atoms (Fig. 7) as compared to the ground state (Fig. 6). In the bridgehead bond of bicyclobutane the picture is more complicated, since, in addition to the flow of charge from the interatomic space, we have a complicated change in strain.

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