

HIDDEN SYMMETRY OR WHY CYCLIC MOLECULES HAVE SO STRANGE FORMS

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Abstract. In this contribution we report on a study of conformation transitions in a cyclohexane in the temperature range from -100° to 1200°C . The bond charge molecular dynamics was used. To explain the results obtained, we have developed a method with the help of which the theory of electron pairs repulsion can be enlarged and be applied to cyclic molecules. The approach created reveals a hidden symmetry of spatial electronic structure which, in general, does not coincide with the symmetry of a visible atomic structure. However this spatial electronic structure presets an atomic structure and explains why a cyclohexane molecule has so unusual conformations as a boat and a chair.

1. Cyclohexane conformations

At first, cyclohexane (C_6H_{12}) was depicted as a molecule having a plane carbon ring. Later it was established that it has highly symmetric ‘chair’ configuration which belongs to the symmetry group D_{3d} (Fig. 1a). Here [1] four carbon atoms lie in one plane, two others are disposed bilaterally along the plane, all the valence angles CCC are tetrahedral, and all the C-H bonds of neighboring methylene groups are disposed in chess order with respect to each other. From twelve C-H bonds, six bonds are axial and parallel to the symmetry axis of the third order; other six bonds are equatorial. Geometric parameters of the molecule are:

$$r(\text{C-C})=1.54 \text{ \AA}, \quad r(\text{C-H})=1.09 \text{ \AA}.$$

The chair is a stable conformation of cyclohexane. Another conformation is a boat (or a bath) which belongs to the symmetry group C_{2v} (Fig. 1b). It is unstable and at room temperature only one molecule from a thousand has a boat conformation. Chemical and physical methods are unable to fix each conformation separately; they see only an average picture. In this paper we report on a study of structure changes of cyclohexane in the temperature range from -100° to 1200°C .

2. Computer simulations

The bond charge molecular dynamics described in detail elsewhere [2] was used. Figure 2 shows the evolution of an initially plane configuration at two extreme temperatures: -100° and 1200°C . Here the large circles represent carbon atoms, the smaller ones refer to hydrogen atoms, and the smallest ones show electron pairs located at the centers of covalent bonds. At -100° the plane configuration transforms into a chair conformation, at 1200° the structure is unstable and the conformations are changed quickly. At intermediate temperature, e.g. 300° , there are possible both conformations (Fig. 3).

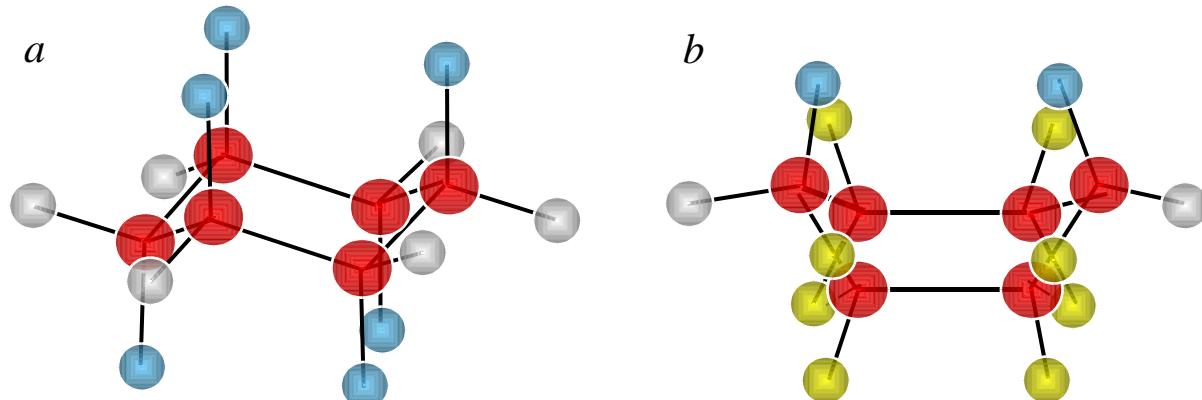


Fig. 1. Structure of a cyclohexane molecule: a) chair conformation, b) boat conformation.
Large spheres are carbon atoms, small spheres are hydrogen atoms.

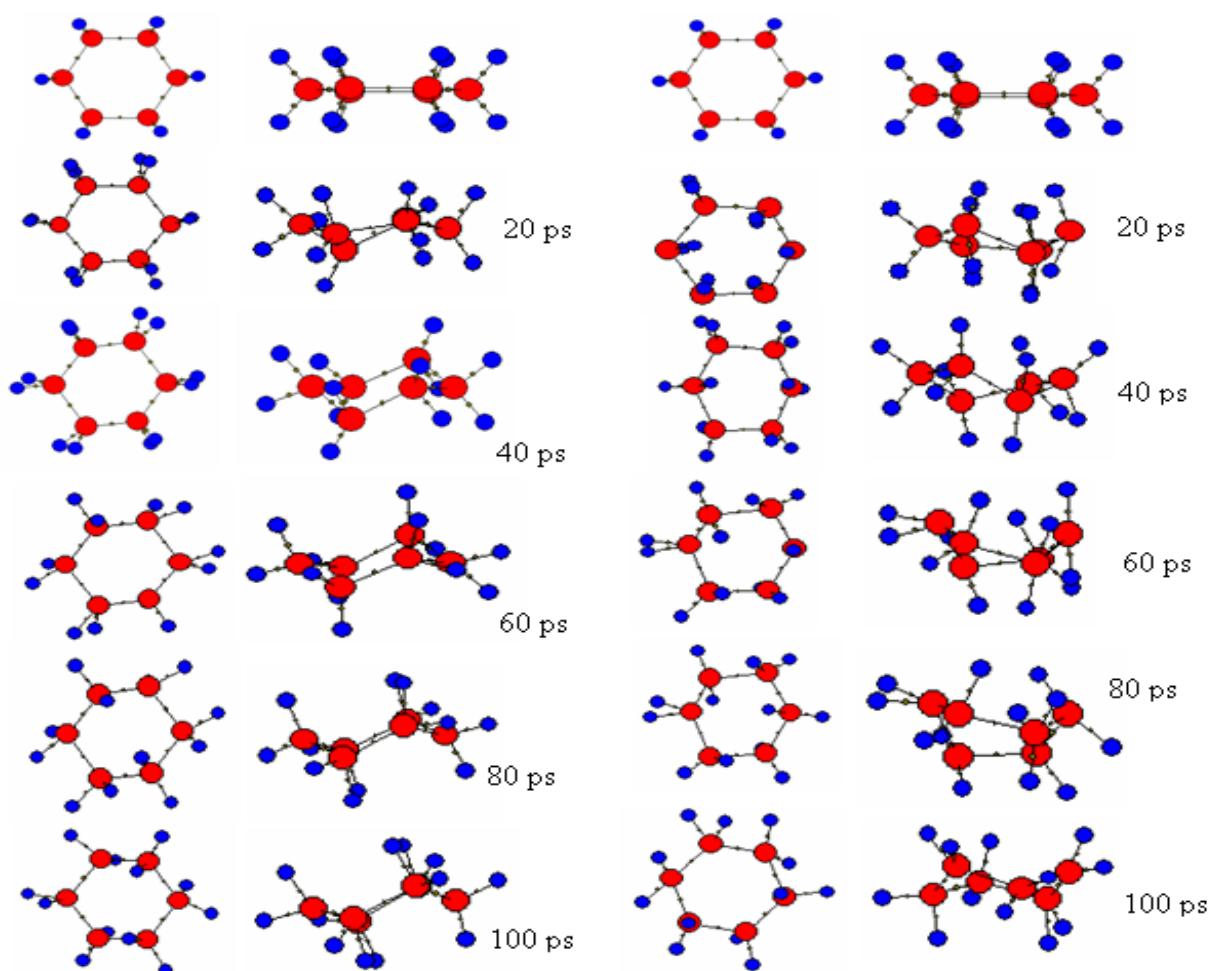


Fig. 2. Cyclohexane conformations at low and high temperatures.

At -100°C there forms a chair conformation (on the left).

At 1200°C the conformations are unstable and change very quickly (on the right).

A close-up of the formation of a chair conformation at a low temperature is given in Figure 4. A close-up of a boat conformation at an intermediate temperature is shown in Figure 5. The ‘boat–chair’ conformation transition at a high temperature is given in Figure 6.

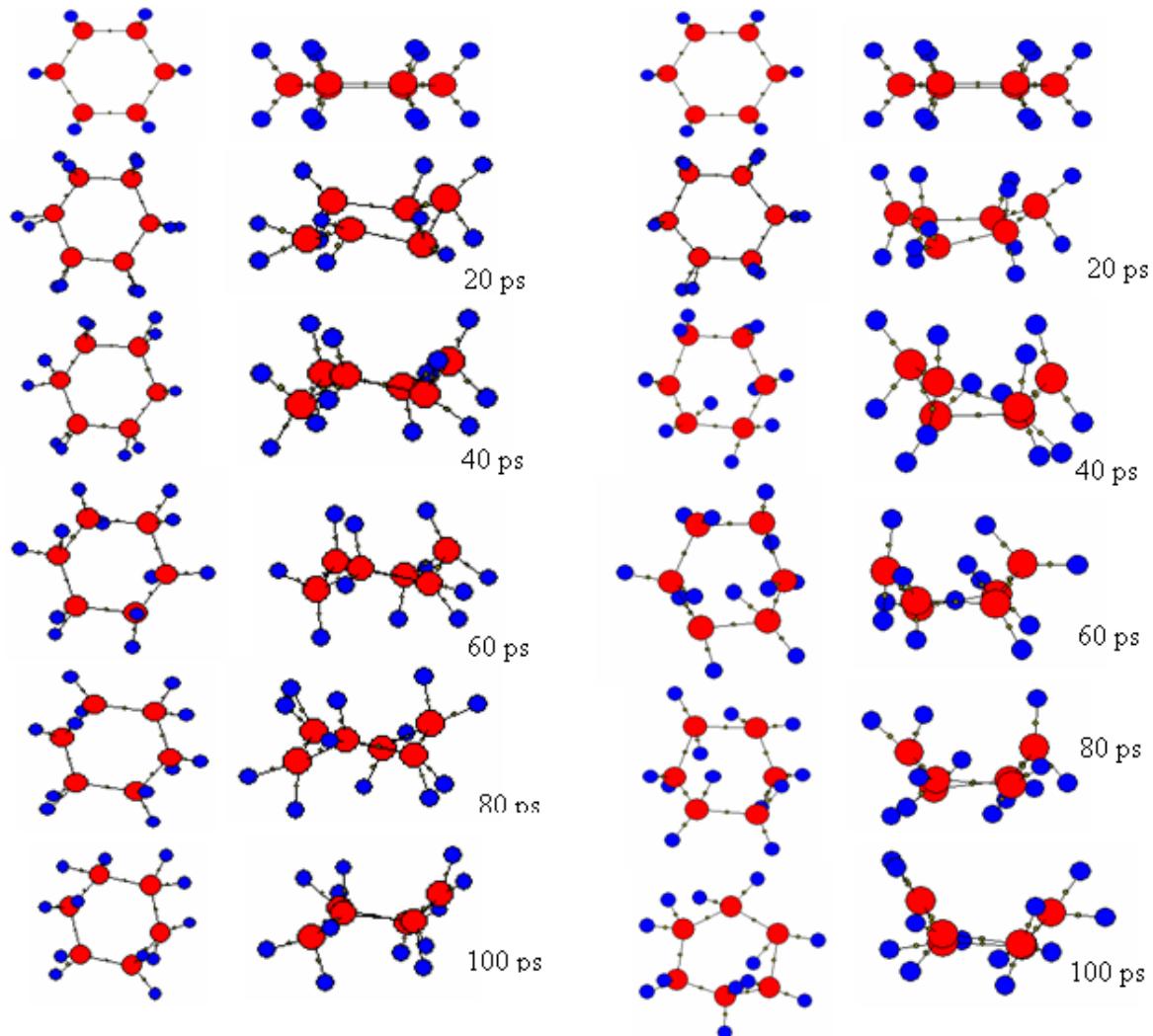


Fig. 3. Cyclohexane conformations at 300°C: a chair conformation (on the left), a boat conformation (on the right).

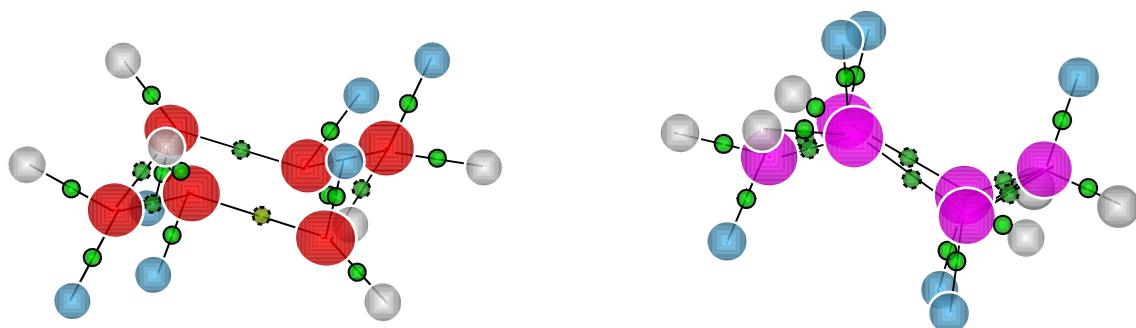


Fig. 4. Formation of a chair conformation at -100°C: 40 ps (on the left) and 80 ps (on the right). Here and below small smooth spheres are the electron pairs located at the centers of H-C covalent bonds; small uneven spheres are the electron pairs located at the centers of C-C covalent bonds.

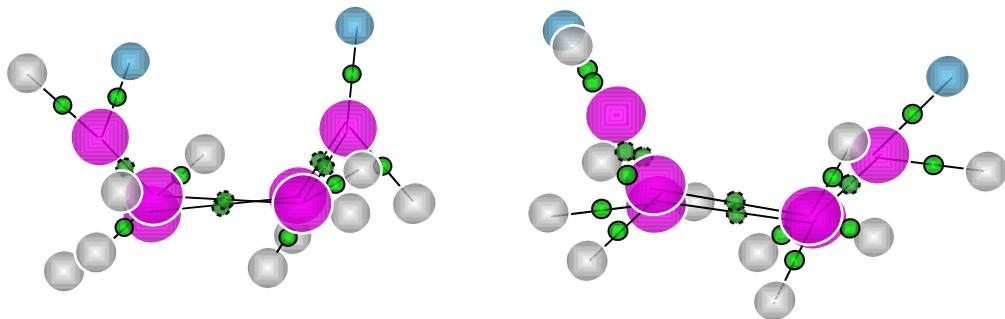


Fig. 5. Vibrations of atoms in a boat conformation at 300°C:
80 ps (on the left) and 100 ps (on the right).

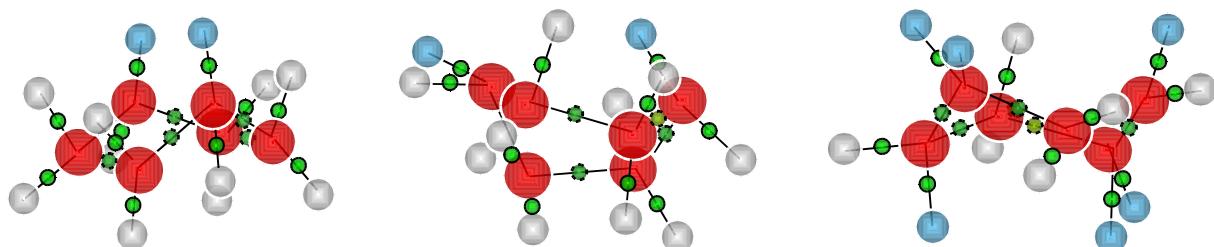


Fig. 6. Boat-chair conformation transition at 1200°C:
40 ps (on the left), 80 ps (at the center) and 100 ps (on the right).

3. Hidden symmetry: space structure of electron pairs

As it was discussed in details [3], in 1940 Sidgwick and Powell formulated the following rule: electron pairs arrange themselves inside the valence band of an atom into such configuration which ensures their maximal removing from each other. The theory allows explain and predict stereochemical properties of molecules. But these molecules are rather simple, for example methane, which has four electron pairs forming a tetrahedron. For this reason the entire molecule CH_4 also has the form of a tetrahedron.

Let us extend this theory and apply it to cyclohexane. In a cyclohexane molecule one can set off a building block in the form of a tetrahedron (Fig. 7). In essence, this cyclic molecule is a chain of blocks rolled up into a ring; the blocks having two common apexes.

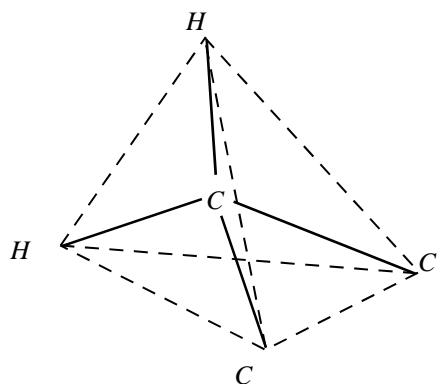


Fig. 7. Building block of cyclohexane.

Consider, for example, a chair conformation. Draw a plane through the electron pairs of carbon atoms (Fig. 8). The electron pairs form in this plane a ring in the form of a regular hexagon (Fig. 9.1). Build perpendicularly to the plane a regular, right six-angle prism; its edges passing through the electron pairs (Fig. 9.2). Cut the prism along one of its lateral edges (Fig. 9.3). Unroll the lateral surface of the prism upon a plane normal to the prism base (Fig. 9.4). Add the electron pairs of carbon-hydrogen bonds to this pattern. Then one obtains the scanning of the cyclohexane electronic structure (Fig. 10).

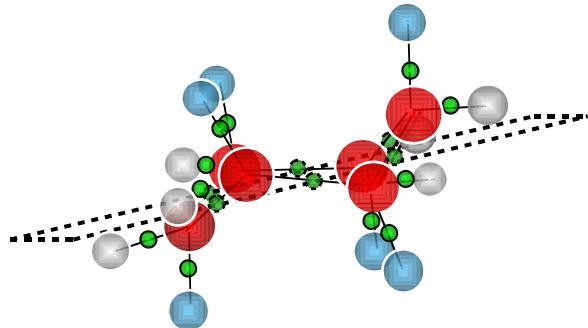


Fig. 8. Chair conformation; the plane shown by dotted lines passes through electron pairs of carbon-carbon bonds.

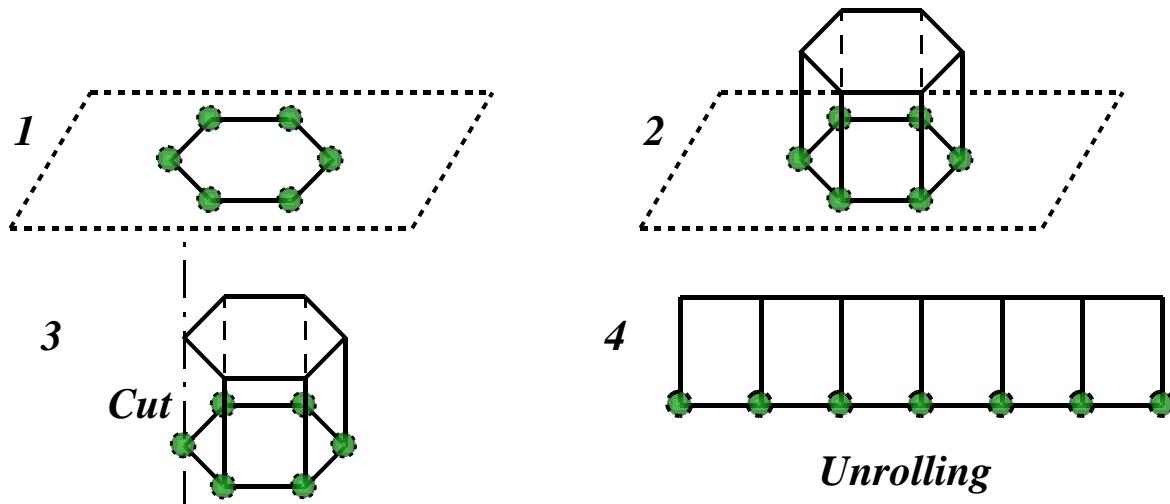


Fig. 9. Algorithm for revealing the hidden electronic symmetry of cyclohexane in a chair conformation.

The all-important result is that such procedure reveals the **hidden symmetry** of electron pairs. It should be emphasized that the algorithm developed gives the symmetry of spatial electronic pattern which does not coincide with that of atomic one (Fig. 11a). However this electronic pattern defines the atomic structure (Fig. 11b) and explains why a cyclohexane molecule has such unusual form as a chair.

In a similar manner consider a boat conformation. In contrast to a chair conformation, here the electron pairs of carbon atoms do not lie in one plane, but in two intersecting planes (Fig. 12). As a result, this leads to the change of electronic and atomic pattern (Fig. 13), however the symmetry of electronic and atomic structure coincides (group C_{2v}).

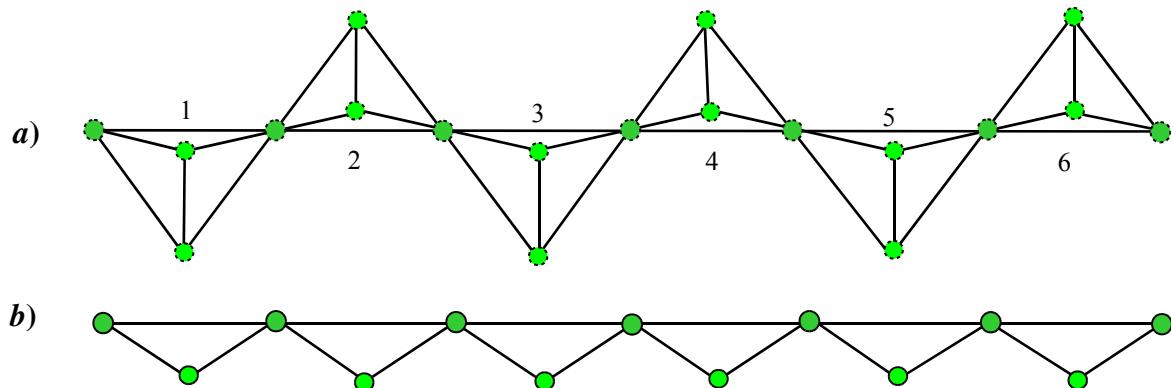


Fig. 10. Electron pairs tetrahedra of cyclohexane in a chair conformation (scanning on a plane); a) view from the outside of a prism, b) scanning view from above.

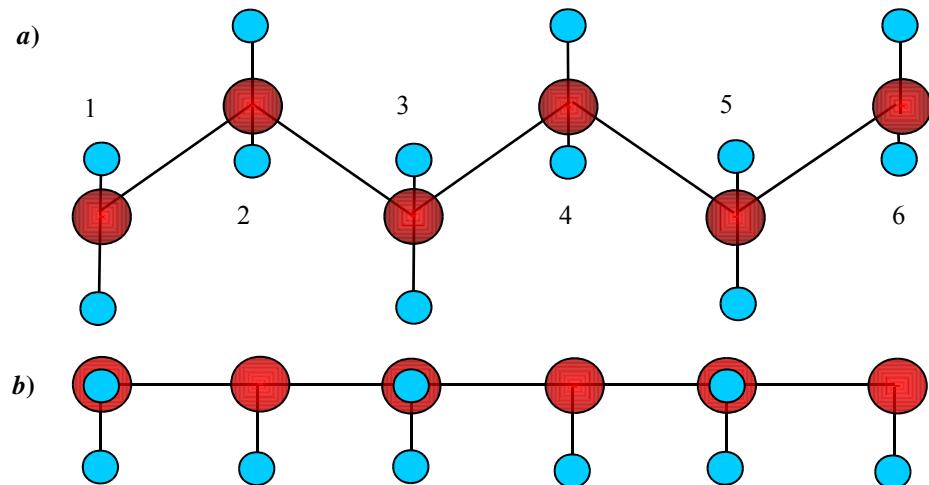


Fig. 11a. Cyclohexane in a chair conformation (scanning on a plane); a) view from the outside of a prism, b) scanning view from above.

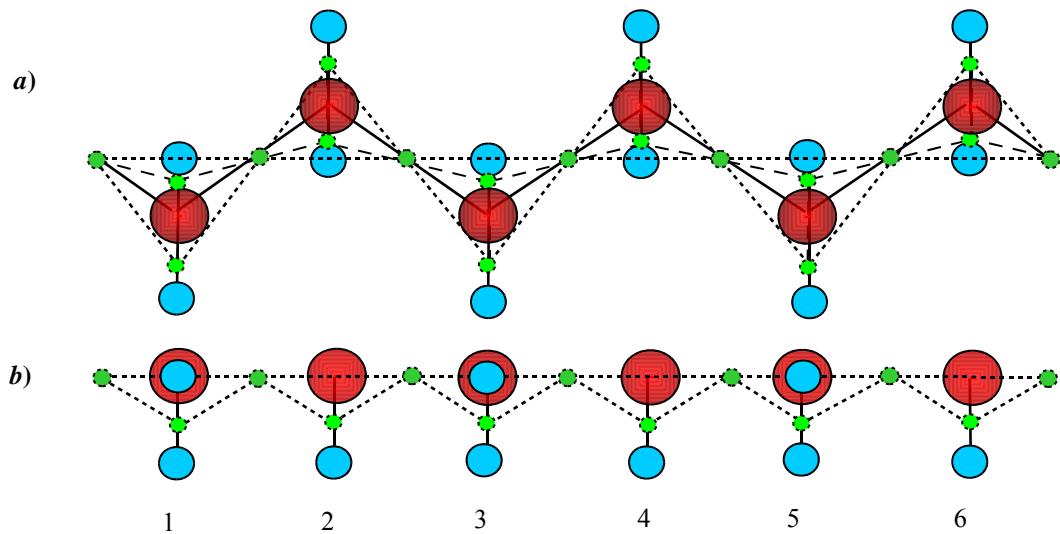


Fig. 11b. Electronic and atomic pattern of cyclohexane in a chair conformation (scanning on a plane) – a) view from the outside of a prism, b) scanning view from above.

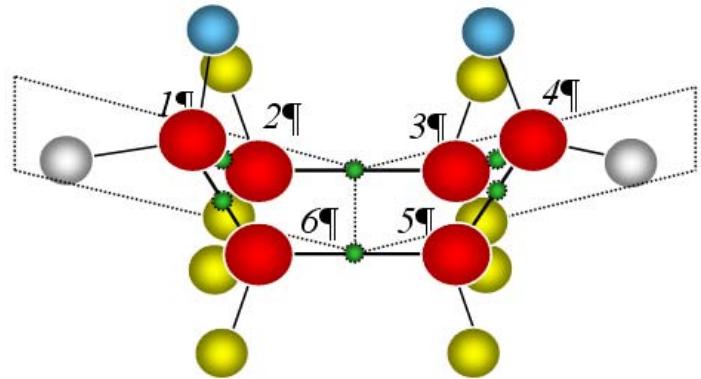


Fig. 12. Boat conformation. Dotted lines are traces of planes, in which electron pairs of carbon atoms are lying.

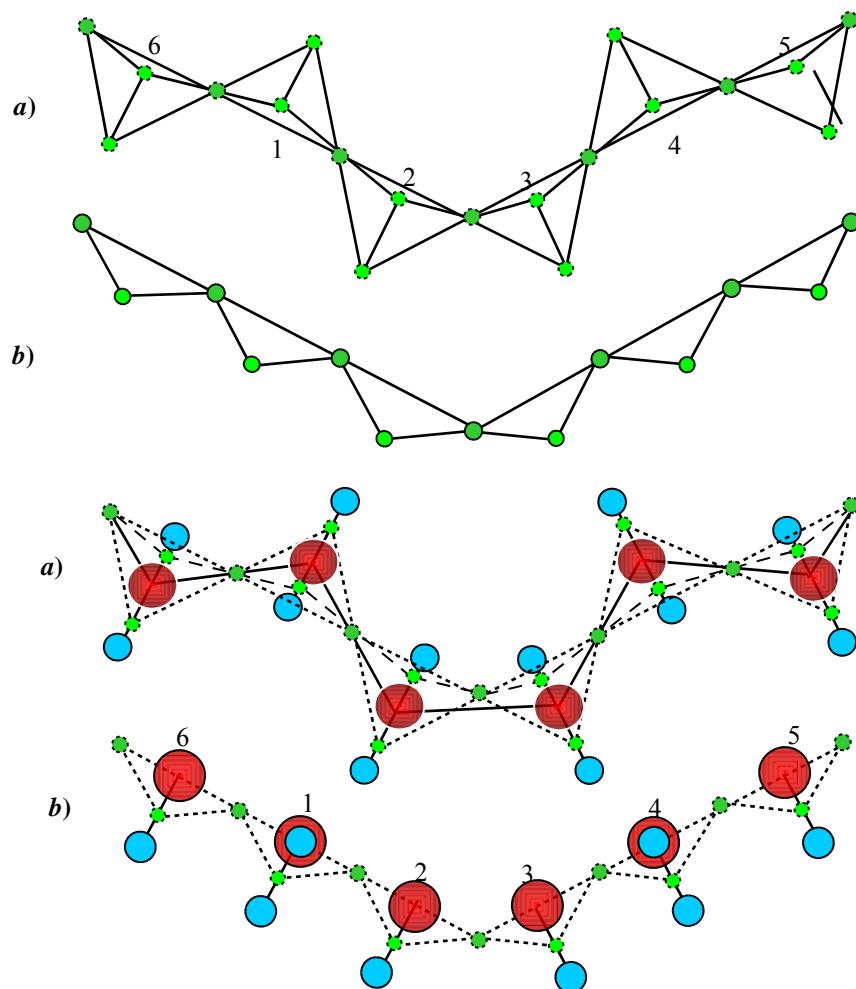


Fig. 13. Above the electron pairs tetrahedra of cyclohexane in a boat conformation are shown (scanning on a plane) – a) view from the outside of a prism, b) scanning view from above. At the bottom of the figure, electronic and atomic pattern of cyclohexane in a boat conformation are given (scanning on a plane) – a) view from the outside of a prism, b) scanning view from above.

4. Mechanism of conformation transitions

It is generally accepted in textbooks that the conformation transition ‘chair–boat’ realizes according to the following mechanism. At first the down corner of a chair raises forming an un-

stable “semi-chair” which corresponds to the maximum of the energy curve (Fig. 14). Further movement of the corner creates a boat conformation and decreases the energy, but the boat conformation is less stable than the chair one. This supposition is a basis for customary consideration of chain molecules.

However, Man proposes, but God disposes. From the molecular dynamics results obtained, it follows that the conformation transition is realized due to the process which resembles rather torsion of the plane where four carbon atoms lie (Fig. 6b).

Consider the problem of conformation transitions in the context of the stability theory [4]. To bend a hexagon around any axis of C_6 symmetry, it is necessary to apply forces similar to those shown in Figure 15a. If the bending leads to equilibrium state, one obtains a boat conformation. In terms of the stability theory, it means the stability loss of a first harmonic (mode). One may imagine also the stability loss of a second harmonic (mode) as shown in Figure 15b. In this case one obtains a chair conformation. The preference depends on elasticity moduli and applied forces. The forces arise due to electron pairs interaction as well as due to thermal vibrations of atoms (thermal forces).

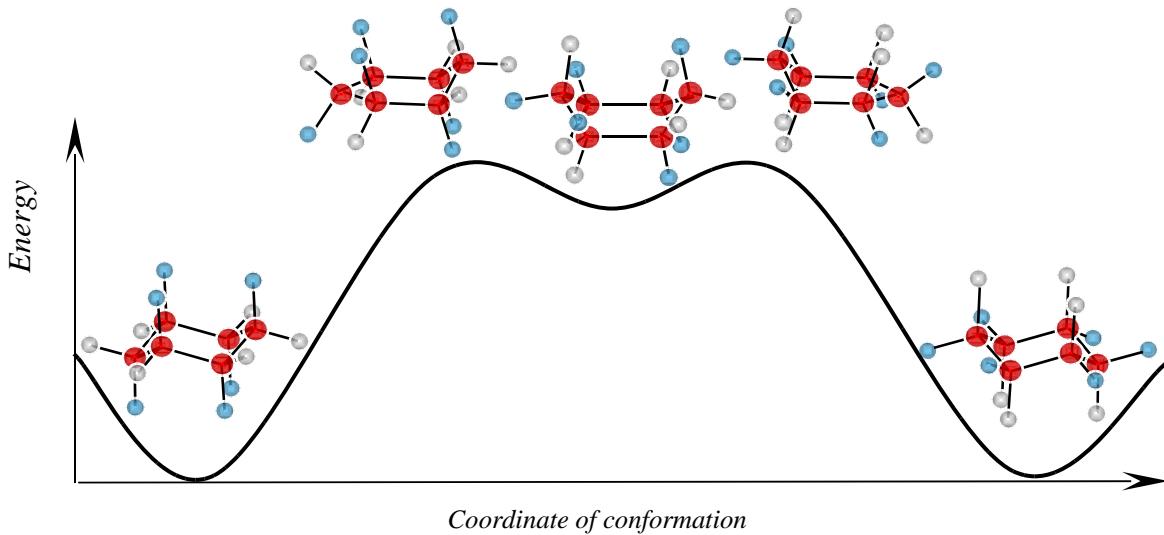


Fig. 14. Change of transition energy along a coordinate of conformation.

Let us estimate these forces. The geometric parameters of a cyclohexane molecule are:

$r(C-C)=1.54 \text{ \AA}$, $r(C-H)=1.09 \text{ \AA}$. According to [3] the bond charges for C-C and C-H bonds are equal to $0.169 e$ and $0.077 e$, respectively, where e is the electron charge. Consequently the electrostatic interaction energy for electron pairs of C-C bonds equals $\sim 0.28 \text{ eV}$, whereas the electrostatic interaction energy for electron pairs of C-C and C-H bonds is only $\sim 0.003 \text{ eV}$. The thermal motion energy is kT . At -100° , 300° , and 1200°C it is $\sim 0.114 \text{ eV}$, $\sim 0.05 \text{ eV}$, and $\sim 0.1 \text{ eV}$, respectively. Therefore at low temperatures, where a molecule has a regular form, this structure is supported by electric forces. At high temperatures, the thermal motion of hydrogen atoms is the main destabilizing factor (Fig. 6b). This motion changes H-C-H valence angles and, as a consequence, the regular form of the molecule.

Thermal motion is chaotic one. From Figure 15 it is seen that the second mode is more chaotic than the first one, which is highly correlated. Consequently, if the temperature increases, the appearance of the second thermal mode becomes more probable than the first thermal one. In essence, the second mode is torsion and this circumstance must be taken into consideration in any satisfactory explanation of the conformation transitions.

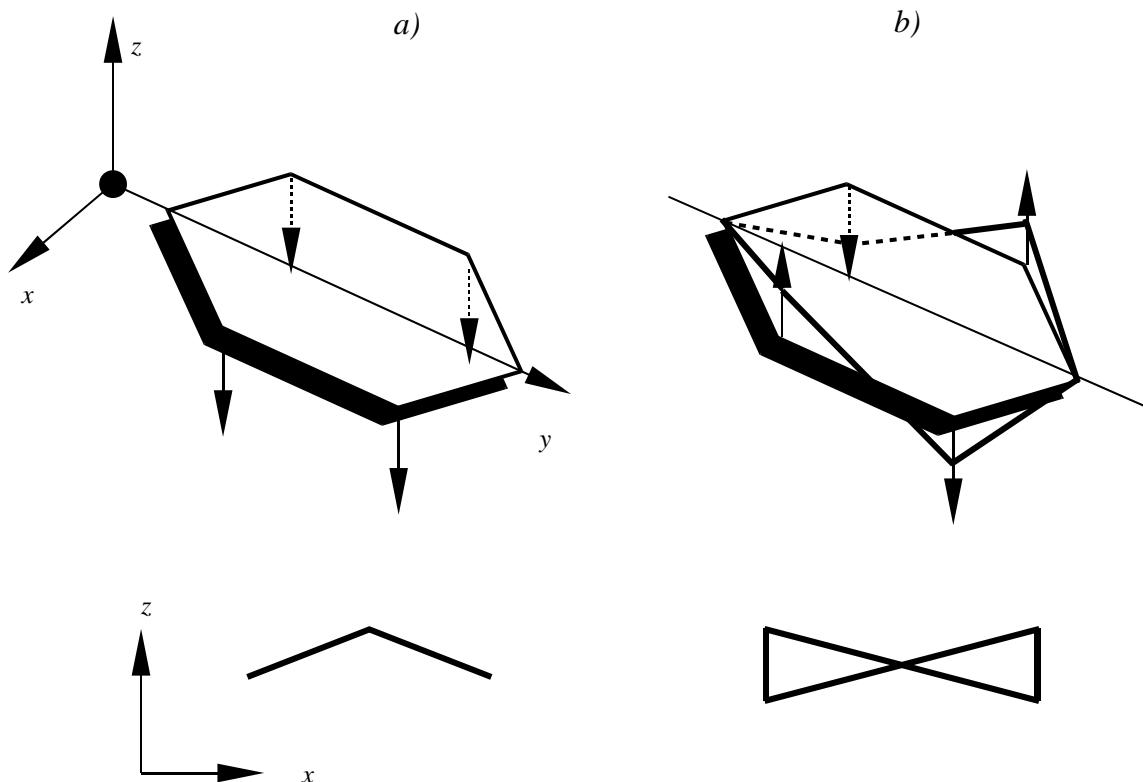


Fig. 15. Stability loss of a hexagon under the action of applied forces.

5. Conclusion

We have developed an algorithm with the help of which the theory of electron pairs repulsion can be enlarged and be applied to cyclic molecules. The approach created reveals a hidden symmetry of spatial electronic structure which, in general, does not coincide with the symmetry of a visible atomic structure. However this spatial electronic structure presets an atomic structure and explains why a cyclohexane molecule has such unusual conformations as a boat and a chair.

References

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