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ON THE SYMMETRY OF BENZENE MOLECULES AND RELATED COMPOUNDS

The article presents considerations on the basis of which benzene molecules, by their symmetry, should be assigned not to the holohedral class $m \cdot 6 : m$ of the hexagonal system, as has been generally accepted up to now, but to the class $\bar{6} \cdot m$ of the trigonal system. A similar change in symmetry is also envisaged for the molecules of all other compounds of the type $C_{2n}H_{2n}$. The author's proposal makes it possible to understand more deeply why compounds of the series C_4H_4, C_8H_8, $C_{12}H_{12}$, ..., in their properties, differ sharply from compounds of the series C_6H_6, $C_{10}H_{10}$, $C_{14}H_{14}$, ...

Almost 100 years have passed since Kekulé proposed his world-famous formula for benzene (^{1}). At the present time most chemists unreservedly accept that, in complete agreement with Kekulé' s formula, in the benzene molecule the six carbon atoms are situated at the vertices of a plane regular hexagon. As for the three double bonds appearing in the benzene formula, opinions concerning them still differ.

In our time, the conception of the benzene molecule and of other analogous cyclic compounds set forth in the work of E. Hückel (^{2}) is widely known. In this work, in particular, an explanation is given of why cyclic compounds of the series C_4H_4, C_8H_8, $C_{12}H_{12}$, ... cannot possess the properties typical of aromatic compounds of the series C_6H_6, $C_{10}H_{10}$, $C_{14}H_{14}$, ..., despite the fact that the molecules of compounds of both these series have an analogous structure. Hückel bases his quantum-theoretical reasoning on the following assumptions:

1. All carbon atoms in the molecules of cyclic compounds of the type $C_{2n}H_{2n}$ lie at the vertices of a plane regular $2n$-gon. The hydrogen atoms are situated at the vertices of a concentric $2n$-gon in such a way that the straight lines joining the carbon atoms with the corresponding hydrogen atoms pass through the common center of both polygons.
2. All carbon atoms (as well as all hydrogen atoms) are mutually equivalent in all respects and, in particular, all have the same electronic environment. At the same time it is considered known that each carbon atom has four

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

"chemical" electrons in the L-shell and two electrons in the K-shell that do not take part in chemical reactions. These two electrons are not taken into account in Hückel' s arguments. Each hydrogen atom has a single "chemical" electron, although it is situated in the K-shell.

3. The single bonds between atoms in the compounds under consideration are produced by pairs of "chemical" electrons. As is easy to calculate, in molecules of the type $\mathrm{C}_{2n}\mathrm{H}_{2n}$ they are present in more than sufficient quantity for the formation of all single bonds.

On the basis of these assumptions Hückel depicts the molecules of compounds $\mathrm{C}_{2n}\mathrm{H}_{2n}$, in particular the benzene molecule, as is shown in the upper line of Fig. 1, where paired electrons are marked by dots and unpaired (π-electrons) by asterisks. In Hückel' s opinion, precisely these π-electrons are responsible for the specificity of the properties of the substances under consideration. In Ingold' s book (^{3}) the totality of the π-electrons of the benzene molecule—

the antibond is represented as a single cloud of indefinite form, enveloping the molecule on both its sides.

Hückel and a number of other authors (references to them may be found in (3)) assert that the benzene molecule has "hexagonal symmetry," without specifying which of the seven possible hexagonal classes is meant in the given case. Looking at the image of the benzene molecule shown in Fig. 1, it is not difficult to conclude that, by its symmetry, it ought to belong to the holohedral class $m \cdot 6 : m$ of the hexagonal system, and that the molecules of the entire series C_4H_4, C_6H_6, C_8H_8, $C_{10}H_{10}, \ldots$ respectively belong to the classes $m \cdot 4 : m$, $m \cdot 6 : m$, $m \cdot 8 : m$, $m \cdot 10 : m, \ldots$

Fig. 1. Structure of ring molecules of compounds $C_{2n}H_{2n}$ according to E. Hückel (first row). Symmetry of the same molecules in the generally accepted representation (second row). Symmetry formulas according to A. V. Shubnikov (third row)

Fig. 2. Structure of ring molecules of the compound $C_{2n}H_{2n}$ according to A. V. Shubnikov (first row). Symmetry of the same molecules in the generally accepted representation (second row). Symmetry formulas according to A. V. Shubnikov (third row)

In Fig. 1 these classes are represented, as is generally accepted, by stereographic projections of the corresponding symmetry elements. From these projections it is evident that, in their symmetry, the compounds of the series C_4H_4, C_8H_8, $C_{12}H_{12}, ...$, contrary to reality, should not differ in any essential respect from the compounds of the series C_6H_6, $C_{10}H_{10}$, $C_{14}H_{14}, ...$

In order to eliminate the contradiction just noted, we set ourselves the task of showing that, relying on the same premises as Hückel, it is possible to assign to the molecules $C_{2n}H_{2n}$ a different symmetry, and one that, in our view, corresponds more closely to reality. For this purpose it is sufficient to arrange the π-electrons, denoted by Hückel with asterisks, alternately above and below the carbon plane, at equal distances from it. In Fig. 2 such an arrangement is shown schematically by white and black circles. The white circles correspond to three electron clouds directed, say, upward from the plane of the carbon hexagon, and the black circles to three clouds directed downward from this plane. It is not difficult to verify that, with the indicated arrangement of the π-electrons, all carbon atoms and, correspondingly, all hydrogen atoms retain their equivalence, remaining in their places at the vertices of plane regular polygons.

It is easy to check that the structural formulas of the compounds $C_{2n}H_{2n}$ proposed by us must now, according to their symmetry, belong to the classes $\overline{4} \cdot m$, $\overline{6} \cdot m$, $\overline{8} \cdot m$, $\overline{10} \cdot m, ...$, and the formula of benzene, in particular, to the class $\overline{6} \cdot m$ not of a hexagonal, but of a trigonal system.

From the stereographic projections, given in Fig. 2, of the symmetry elements belonging to the molecules C_4H_4, C_6H_6, C_8H_8, $C_{10}H_{10}, ...$, it is seen that in the molecules of the unstable compounds C_4H_4, C_8H_8, $C_{12}H_{12}, ...$ there is no center of symmetry, whereas in the molecules of stable compounds (in particular, benzene) C_6H_6, $C_{10}H_{10}$, $C_{14}H_{14}, ...$ a center of symmetry is present.

The question of why centrosymmetric molecules are more stable than non-centrosymmetric ones remains open.

In conclusion we note that the idea of assigning the benzene molecule to the trigonal system arose for us while reading article (^{4}). We express here our gratitude to the author of this article, Z. N. Parnes, for indicating the literature cited above.

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Note: Figure translations are in progress. See original paper for figures.