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Abstract

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THREE-CENTER ORBITS AND THE STRUCTURE OF CYCLOPROPANE AND OTHER COMPOUNDS WITH THREE-MEMBERED RINGS

The idea that three-center orbits, including the atomic orbits of three atoms, are realized in molecules arose in connection with the problem of the structure of borohydrides and other electron-deficient compounds that do not fit within the framework of ideas about ordinary chemical bonds localized between two atoms (^{1}). Analogous three-center orbits are also assumed in π-complexes formed by double bonds with positive ions that provide a third empty orbit (in addition to the two atomic orbits forming the π-bond (^{2})). In essence, the bonds between a platinum atom and an ethylene molecule in compounds of the Zeise-salt type (^{3}) are also reducible to three-center orbits. These examples, belonging to classes of chemical compounds that differ greatly from one another, show that the formation of three-center orbits is not an exceptional case, but is rather widely distributed in various molecules.

We believe that such orbits may also be realized in many other cases besides those listed above, and that by invoking the concept of three-center orbits one can approach an explanation of the structure of a number of other molecules. This applies first of all to a series of compounds with an insufficient number of electrons, formed upon the addition of a proton to valence-saturated molecules. It is known that the reaction $H_2 + H^+ = H_3^+$ is accompanied by the liberation of 70 ± 9 kcal/mole (^{4}), so that a triatomic complex H_3^+ with two electrons can exist. V. L. Tal' roze and co-workers (^{4}) discovered the methonium ion CH_5^+, in which the carbon atom is bonded to five hydrogen atoms; moreover, in the reaction $CH_4 + H^+ \rightarrow CH_5^+$, 121 ± 9 kcal/mole is liberated. For H_3^+, the assumption of the realization of three-center orbits is the only possible and generally accepted one. We believe that an analogous situation also obtains in CH_5^+. There is hardly any other way to explain the structure of CH_5^+. On the other hand, when the concept of three-center orbits is used, the difficulties are largely removed. We suppose that three C–H bonds (the CH_3 group) are ordinary covalent two-electron and two-center bonds.

In addition to these bonds, the C atom has one more orbit and one electron, and the two attached H atoms each have one more orbit, so that a three-center orbit

Structure (I)

Figure 1: Structure (I)

Structure (II)

Figure 2: Structure (II)

may arise, which may be of either the central or the open type (according to the classification of Eberhardt, Crawford, and Lipscomb (^{1})), depending on the ratio of the integrals $\gamma_{\mathrm{H}\ldots\mathrm{H}}$ and $\gamma_{\mathrm{C-H}}$. Two electrons are located on this three-center orbit (one from the C atom and the other from one of the H atoms), whereas the second proton

has no electron). In this case the molecule has structure (I).

In addition to electron-deficient compounds, three-center orbitals can, in our opinion, also occur in other molecules—especially those containing three-membered rings. It is known that such compounds as, for example, cyclopropane and its analogues are characterized by certain features that distinguish them from other alicyclic organic compounds. This is most clearly manifested in the fact that compounds containing a cyclopropane ring show some similarity to unsaturated compounds. This applies, for example, to addition reactions, as well as to a number of anomalies that can be explained only by introducing the assumption of "conjugation" of the cyclopropane ring with attached double bonds or phenyl groups, as in diene conjugated systems. It seems to us that the existing hypotheses concerning the structure of cyclopropane, in which the presence is postulated of three σ-bonds C—C directed along the sides of the triangle (with a large deviation from the directions of maximum concentration of the wave functions of the corresponding bonding hybrid σ-orbitals), do not make it possible to give a satisfactory explanation of the anomalies listed above. There are indications in the literature that the cyclopropane ring behaves like a double bond and therefore can be conjugated with other double bonds; however, the physical reason remains unclear for the conjugation of π-bonds with the σ-bonds of the ring, which is much more effective than in other cases of σ-π conjugation. This prompts a search for other hypotheses that could better convey the properties of three-membered rings.

The specific configuration of a three-membered ring, with angles of 60°, suggests the possibility that three-center orbitals may also occur in this case. If one assumes that two C—H bonds are formed by each carbon atom in cyclopropane by means of two hybrid atomic orbitals, then each C atom still has two orbitals remaining. The fact that the HCH angle is 120° (^{5}) permits one to assume that hybridization takes place in a plane perpendicular to the plane of the ring, so that for the bonds in the ring there remains one hybrid sp^2-orbital directed from the C atom toward the center of the ring (II), and a π-orbital lying in the plane of the ring, perpendicular to the plane HCH.

The described σ-orbitals are quite suitable for the formation of ordinary three-center orbitals of the "central" type. Four electrons can occupy the two lowest orbitals—the bonding and the nonbonding ones. The remaining two electrons can, as we believe, occupy the lowest of the three-center orbitals of another type, arising from the three π-orbitals of the C atoms. Such orbitals are not encountered in borohydrides, but the possibility of their formation seems quite probable. This is a question of the interaction of π-orbitals whose axes are located in one plane at angles of 120° to one another, with the formation of a single molecular orbital encompassing all three C atoms along the circumference described around the triangle CCC. It is natural to think that this interaction is weaker than

leading to the formation of an ordinary three-center σ-orbital of the central type. Therefore only one lower three-center π-orbital turns out to be occupied. The π-orbital described differs from the ordinary three-center σ-orbital in that in the latter the electron density is concentrated in the directions going from the C atoms toward the center of the ring and at the center itself, whereas in the three-center π-orbital the electron density is distributed along a circumference enclosing the triangle of C atoms. Such a distribution of electron density differs from that predicted on the basis of the usual ideas about two-center σ-bonds in cyclopropane in that, with ordinary bonds, the electrons are located exclusively along the perimeter of the triangle, while in the picture we propose, owing to the presence of "central" three-center orbitals occupied by four electrons, a considerable part of the electron density is found not in the region of the perimeter but inside the triangle. The conjugation of the cyclopropane ring with attached double bonds is evidently due to the presence of a three-center π-orbital interacting with the π-orbitals of the double bonds. In this case, however, the interacting orbitals are not situated in strictly parallel planes (which is altogether impossible if the bond $C{-}CH{=}CH_2$ or $C{-}Ph$ makes an angle of 60° with the plane of the ring). But this, as is known, is not an obstacle to conjugation(6). The idea of conjugation of a three-center π-orbital is not in contradiction with the sometimes advanced supposition that conjugation in cyclopropane derivatives occurs through "opening" of the ring, which is represented by means of the following valence schemes brought under consideration:

$$\mathrm{CH_2{-}CH{=}CH{-}\dot{C}H_2}$$

$$\mathrm{\dot{C}H_2}$$

As is shown by consideration of π-complexes(2), such valence schemes correspond, although in a less explicit form, to a three-center orbital in the molecular-orbital method.

The ideas set forth should apply not only to cyclopropane, but also to such analogs of it as ethylene oxide or ethylenimine.

Another example of a molecule that may be based on three-center orbitals is iron tetracarbonyl, $Fe_3(CO)_{12}$. Braun(7) already indicated that the diamagnetism of this compound can be explained only if one assumes the presence of three-center orbitals Fe—Fe—Fe. However, Braun supposed that the molecule has the structure $(CO)_3Fe(CO)_3Fe(CO)_3Fe(CO)_3$, and the three-center orbitals he adopted were of an "open" type. At present it has become known that the molecule does not have the structure given above, but contains a triangle of Fe atoms(8). In this case it is natural to retain the idea of three-center orbitals with the electron distribution given by Braun, leading to diamagnetism, but with orbitals not of the open type but of the central type—as in cyclopropane.

The probable existence of three-center orbitals in cyclopropane and $Fe_3(CO)_{12}$ gives grounds for supposing that this type of orbital occurs more often than was previously assumed, especially in compounds with three-membered rings.

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