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# Hybridization in Some Three-Membered Ring Organic Molecules

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The molecular structures of some simple three-membered ring compounds, cyclopropane, cyclopropanone, ethylene oxide and ethylenimine, were studied by means of the orbital interaction between the fragments of a molecule. The relation between the carbon-carbon distance and the bending angle of the carbon-hydrogen bonds in ethylenic part of the three-membered rings is attributed primarily to the greater extent of mixing of the unoccupied $\pi$-like MO of ethylenic fragment into the occupied MO's of rings. The increase in the bending angle as going from ethylene oxide to cyclopropane is interpreted in terms of the interaction of an occupied $\sigma$-like orbital with the unoccupied $\pi$-like orbital of ethylenic fragment through the overlap with the orbital(s) of the residual part of rings. INDO MO and localized orbital calculations support the orbital interaction scheme. The same conclusion is derived also from the electrostatic theory of molecular geometries.

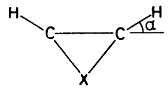
The differences in the structures of some three-membered ring molecules containing sulfur can be rationalized from the viewpoint of orbital interaction between the fragments, generated by a partitioning of the rings.[1] Thus, the long carbon-carbon bond in ethylene episulfone (1.590 Å)[2] in comparison with that in ethylene episulfide (1.492 Å)[3] was ascribed to the stronger interaction between ethylenic fragment and $SO_2$ than that between ethylenic fragment and sulfur orbitals. Although such an analysis is crude, it provides us with a theoretical insight into molecular geometry and suggests that, in some cases, the structure of molecules can be predicted simply by investigating the mode of orbital interaction between fragments.[4] In addition, the concept of orbital interaction primarily introduced in the theory of intermolecular interactions could be further extended to various chemical problems concerning the structure of molecules.[5]

We have developed a method for discussing the differences in the hybridized states of carbon atom in some simple three-membered ring molecules. The structures of cyclopropane, cyclopropanone, ethylene oxide and ethylenimine are given in Table 1.[6] The angle $\alpha$, determined by the methylene plane and the carbon-carbon bond axis, increases with an increase in the carbon-carbon bond distance. The general tendency of the change in the bond distances with the change in hybridized states was studied by Bent, based on experimental observations.[7] The relation between the angle $\alpha$ and the bond distance of three-membered rings may be of interest for an MO theoretical study, since we frequently encounter similar problems in organic and inorganic chemistry.

Table 1. Molecular structures

| | C–C Distance | Bending angle $\alpha$ |
|---|---|---|
| Cyclopropane | 1.51 Å | 30° |
| Cyclopropanone | 1.575Å | 29°7′ |
| Ethylene oxide | 1.472Å | 20°36′ |
| Ethylenimine | 1.48 Å | 20°36′[a] |

a) Assumed.



## Orbital Interaction

Let us consider the orbital interaction in three-membered ring molecules $CH_2CH_2X$ (X=>$CH_2$, >C=O, >NH, >O). We proceed in our usual way first by dividing the ring into two parts, the deformed ethylenic part and X.[1] The rehybridization can appropriately be represented by the "sigma-pi" interaction between the $\sigma$-like part and $\pi$-like part of the ethylenic fragment.[8,9] A stronger interaction indicates a greater rehybridization. The mode of orbital interaction chiefly responsible for the differences in the structure of the rings is illustrated in Fig. 1.[10] We have three significant MO's, $\phi_1$, $\phi_2$ and $\phi_3$, each consisting of the occupied $\sigma$ and the unoccupied $\pi^*$ MO's of the ethylenic fragment and an orbital $\lambda$ of X. All of them are antisymmetric with respect to the plane, bisecting the ring. Figure 2 shows schematically the ways of mixing these three basis MO's to yield the

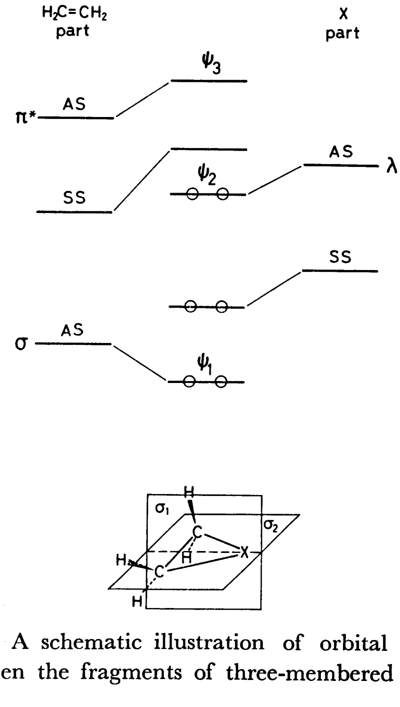


Fig. 1. A schematic illustration of orbital interaction between the fragments of three-membered rings.

Table 2. $\sigma$-$\pi^*$ Mixing in $\psi_1$ and $\psi_2$ ($\psi_2'$)

| | | Coefficient of $\sigma$ | Coefficient of $\pi^*$ | Product of coefficients | Orbital energy($\lambda$) |
|---|---|---|---|---|---|
| Cyclopropane | $\psi_1$ | 0.9462 | 0.0977 | 0.0924 | 2.05 eV |
| | $\psi_2$ | −0.2986 | 0.6295 | −0.1880 | |
| Cyclopropanone | $\psi_1$ | 0.8954 | 0.1336 | 0.1196 | 4.58 eV |
| | $\psi_2'$ | −0.1318 | 0.6093 | −0.0803 | |
| | $\psi_2$ | −0.4042 | 0.3261 | −0.1318 | |
| Ethylene oxide | $\psi_1$ | 0.9531 | 0.0982 | 0.0936 | 0.10 eV |
| | $\psi_2$ | −0.2927 | 0.5336 | −0.1571 | |
| Ethylenimine | $\psi_1$ | 0.9560 | 0.0900 | 0.0860 | 1.73 eV |
| | $\psi_2$ | −0.2779 | 0.5801 | −0.1612 | |
| | | | Orbital energy of $\pi^*$ | | 3.95 eV |

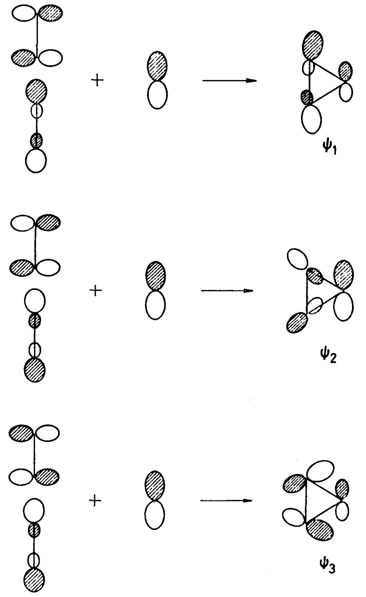


Fig. 2. The modes of orbital mixing.

MO's $\psi_1$, $\psi_2$ and $\psi_3$ of the composite system. The signs of the MO's $\sigma$ and $\pi^*$ were chosen in such a way as for both of them to have positive overlap integrals with the ortital $\lambda$. We then have no phase dislocation in $\psi_1$, one in $\psi_2$, and two in $\psi_3$.

Table 2 gives the products of the mixing coefficients of $\sigma$ and $\pi^*$ in $\psi_1$ and $\psi_2$ (and $\psi_2'$ for cyclopropanone). The MO's were calculated by the INDO MO method,[11] and the expansion of the composite MO's in terms of the MO's of the fragments was carried out in the same way as in our previous works.[12] The remaining composite MO $\psi_3$ is unoccupied and has nothing to do with the electronic structure of the rings.[13] The calculation was carried out on an assumed geometry of cyclopropane, cyclopropanone and ethylenimine, holding the same framework of the ethylenic fragment as that in ethylene oxide. Greater extents of mixing of $\sigma$ and $\pi^*$ are observed in cyclopropane and cyclopropanone than in ethylene oxide and ethylenimine. It is noteworthy that the differences in the magnitude of the $\sigma$-$\pi^*$ interaction are mainly attributed to $\psi_2$. This can readily be understood from the relative energy levels of $\sigma$, $\pi^*$ and $\lambda$ (Table 2) by application of simple MO perturbation theories.[14]

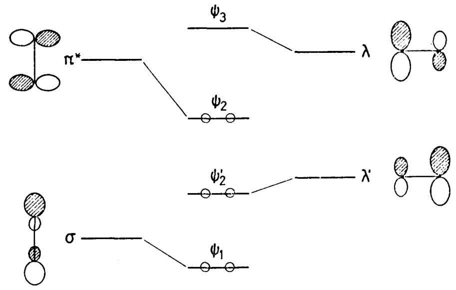


Fig. 3. The orbital interaction in cyclopropanone.

As the level $\lambda$ comes closer to $\pi^*$ in energy ($\varepsilon_\lambda < \varepsilon_{\pi^*}$), the contribution of $\pi^*$ to $\psi_2$ becomes greater. If the MO $\lambda$ happens to be higher than the $\pi^*$ MO, the latter will be the dominant term in $\psi_2$. As a consequence, a greater extent of occupation of $\pi^*$ results in the longer carbon-carbon bond and, at the same time, in a greater "sigma-pi" interaction. In the case of cyclopropanone, the high lying MO $\lambda$ due to the anti-bonding property of the C=O bond would favor a greater contribution of $\pi^*$ to $\psi_2$ and $\psi_2'$ giving rise to the extraordinarily long carbon–carbon distance (Fig. 3). The $\sigma$-$\pi^*$ mixing, however, is compatible with that in cyclopropane. Thus, the increase in $\alpha$ along with the stretching of the carbon-carbon bond can be generalized on the concept of the orbital interaction between the fragments.

## Localized Orbitals

In order to work out the above reasoning quantitatively, we calculated the electron density of cyclopropane and ethylene oxide. Figure 4 shows the density distribution of valence electrons on the molecular plane. For the sake of comparison cyclopropane was subjected to such a deformation that the ethylenic fragment has the same nuclear framework as that of ethylene oxide. The points with the maximum electron densities in the carbon-hydrogen and the carbon-carbon bond regions are plotted. In cyclopropane, the locus of the maximum density extends from the carbon atom with somewhat larger $\alpha$ than that in ethylene oxide. In order to visualize this clearly, we transformed the MO's of cyclopropane and ethylene oxide into the localized orbitals, according to the

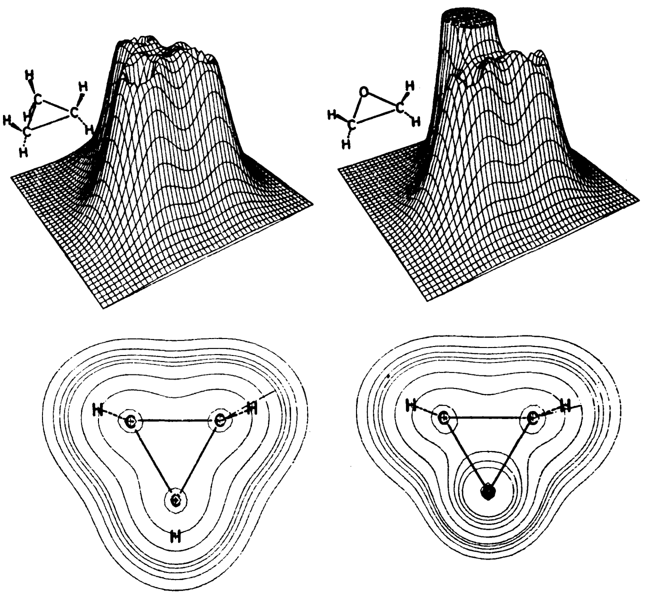
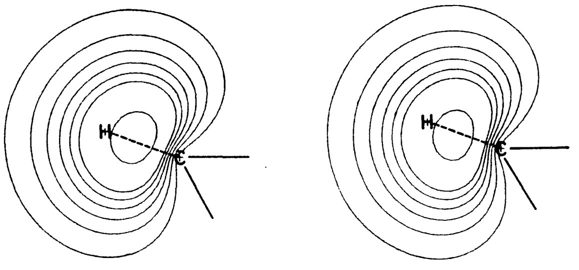


Fig. 4. The electron density distribution in cyclopropane and ethylene oxide.



Cyclopropane Ethylene oxide

Fig. 5. The carbon-hydrogen bond orbitals in cyclopropane and ethylene oxide.

criterion postulated by Edmiston and Ruedenberg.[15)] Figure 5 shows the cross sections of the localized MO's for a carbon-hydrogen bond on the ring plane. It is clear that the carbon-hydrogen orbital of cyclopropane tends to point to the "normal direction", opposing the geometrical constraint imposed upon the ethylenic fragment. To attain maximum bonding, the hydrogen resides in a position of a larger $\alpha$ than that assigned originally.

The localized orbital of cyclopropane is calculated to be

$$\phi_{\text{C-H}}(\text{C}_3\text{H}_6) = 0.390C_s + 0.298C_x + 0.476C_y - 0.148C_z + 0.709H_s - 0.011\lambda + \cdots\cdots$$

and the one for ethylene oxide is given by

$$\phi_{\text{C-H}}(\text{C}_2\text{H}_4\text{O}) = 0.412C_s + 0.299C_x + 0.474C_y - 0.083C_z + 0.711H_s - 0.007\lambda + \cdots\cdots$$

where $C_s$, $C_x$, $C_y$ and $C_z$ indicate the carbon 2s, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals, respectively, and $H_s$ denotes the hydrogen 1s atomic orbital. We see that the bond orbital of cyclopropane has a greater $p_z$ component than that of ethylene oxide. By expanding the orbitals in terms of the MO's of the fragment, we obtain

$$\phi_{\text{C-H}}(\text{C}_3\text{H}_6) = 0.343\sigma + 0.089\pi^* + \cdots\cdots$$

and

$$\phi_{\text{C-H}}(\text{C}_2\text{H}_4\text{O}) = 0.356\sigma + 0.050\pi^* + \cdots\cdots$$

The $\sigma$-$\pi^*$ mixing is more favorable in cyclopropane than in ethylene oxide, as was expected qualitatively from the consideration of the orbital interaction between the fragments.

In the above calculation, cyclopropane was compressed to have an unrealistic ethylenic fragment. In spite of such an artificial choice of atomic coordinates, the results of the calculation appear to be reasonable. Our intuitive interpretation of the differences in the ring structures based on a rather crude orbital interaction scheme seems to be supported by detailed numerical calculations.

## Electrostatic Interaction

In addition to the orbital overlap interaction, the electrostatic effect should be taken into account. With an increase in the electronegativity of X, the charge shift from the carbon atoms to X is strengthened. Accordingly, the electrostatic interaction between the hydrogen atoms and X will be larger as X becomes more electronegative. However, such an electrostatic term in a classical sense, arising from the Coulombic interaction of the net charges, would not be so important in this case, since hydrogens have small net charges in general. Much more important is the binding force exerted on nuclei, originating from the overlap density.[16)] Here, the electrostatic theory of molecular configurations proposed by Nakatsuji[17)] might be useful. As the ethylenic fragment is distorted from planar structure, the exchange force developed by the carbon-hydrogen bonds and the carbon-carbon bond will pull carbon atoms back to the plane defined by the four hydrogen atoms. Thus, the ethylenic fragment is likely to remain in a planar or less distorted structure, opposing the "sigma-pi" interaction.

Chemical interaction between two systems generally causes electron redistributions, accompanied by the formation of new bonds between reaction sites and the weakening of old bonds of reactants to be broken in the course of reaction. The origin of the electron redistribution was analyzed in detail based on the concept of configuration interaction in chemical reactions.[18)] In this case, the $\pi$ like bonding between the carbon atoms of the ethylenic fragment is loosened and new bonds are formed between the fragments. The electron shift from the carbon-carbon bond region to the carbon-X bond regions takes place not through the mutual charge-transfer interaction between the fragments but through the crossing of the AS and SS type MO's.[19)] The overlap density accumulated in the bond region between a carbon and X would attract the carbon toward X. The attracting force gets stronger as the overlap density becomes greater. The difference in the magnitude of the overlap density is determined mainly by the orbital overlap interaction between the $\pi^*$ MO of the ethylenic fragment and $\lambda$ of X. Thus, the overlap density is predominantly governed by the product of the mixing coefficients of

$\pi^*$ and $\lambda$ in $\phi_2$. The mixing in of $\pi^*$ into $\phi_2$ gets poorer as the energy level of $\lambda$ becomes lower (Table 2). The greater the electronegativity of X, the lower the energy level $\lambda$. The greater electronegativity of X indicates the smaller overlap density in the carbon-X bond region and less distorted ethylenic fragment.

## Conclusion

The coupling of a partitioning analysis and an MO expansion procedure seems to be powerful in accurately reproducing MO quantity in a chemically acceptable manner, since we can obtain the exact expressions of the MO's of the composite system in terms of the MO's of the fragments. This kind of approach to the physical and chemical properties of molecular systems would be promising in discussing small but significant differences in similar systems. A simplified interpretation in regard to the difference in hybridization of three-membered rings given here seems to be independent of the approximation employed for the MO calculation.

The present semiquantitative calculation and qualitative concept for interaction revealed that the shorter carbon-carbon distance and smaller bending angle $\alpha$ in simple three-membered ring systems could be ascribed to the greater electronegativity of the central atom or group X. The concept developed here may be applicable to other cases in which changes in valence angles with the change in substituent is noticeable.[20] The assumption of the same bending angle $\alpha$ in ethylenimine as that in ethylene oxide deserves reinvestigation.

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10) Considerable contribution of the MO's with other symmetry properties to the determination of the structure of the rings can be found. This is the case in the three-membered rings where d orbitals are available for X. The mixing of $\sigma$ and $\pi^*$ would be of importance even in these systems.

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