

Tab. 3. Ladungsdichten und Bindungsordnungen des Bacteriochlorins und Metall-Bacteriochlorins.

Atom	Ladungsdichte		Bindung	Bindungsordnung	
	Bact.-Chlorin	Metall-Bact.-Chlorin		Bact.-Chlorin	Metall-Bact.-Chlorin
5	0,949	0,944	5—6	0,66	0,71
6	1,030	1,024	6—7	0,57	0,55
7	1,063	0,959	7—8	0,55	0,53
8	1,040	1,033	8—9	0,74	0,75
18	1,232	1,491	5—18	0,62	0,54
19	1,602	1,590	7—19	0,46	0,49

### Die Ladungsverteilung

Durch die weitere Hydrierung des Chlorins zum Bacteriochlorin hat sich die elektronenziehende Wir-

kung der Pyrrolringe vermindert; als Folge haben sich die Ladungsdichten der Methin-Brückenatome erhöht, sie liegen etwa zwischen denen der  $\alpha$ - und  $\beta$ -Positionen im Chlorin (Tabelle 3).

Die vier Stickstoffatome sind weiter an Elektronen verarmt und die Ladungsverschiebung zur Peripherie hat zugenommen, was sich auch in einer weiteren bathochromen Verschiebung der längstwelligsten Absorptionsbande des sichtbaren Spektrums äußert.

Herrn Prof. Dr. H. H. PERKAMPUS danken wir für die großzügige Unterstützung dieser Arbeit im Physikalisch-Chemischen Institut der Universität Düsseldorf. Die Arbeit wurde durch Mittel der Deutschen Forschungsgemeinschaft unterstützt.

<sup>1</sup> J. V. KNOP u. A. KNOP, Z. Naturforsch. **25 a**, 1720 [1970].

<sup>2</sup> J. V. KNOP u. H. STICHTENOTH, Z. Naturforsch. **27 a**, 639 [1972].

<sup>3</sup> E. RABINOWITCH, Rev. Modern Phys. **16**, 226 [1944].

<sup>4</sup> H. H. INHOFFEN, Die Naturwissensch. **55**, 457 [1968].

<sup>5</sup> H. H. INHOFFEN, J. W. BUCHLER u. R. THOMAS, Tetrahedr. Letters **14**, 1141 [1969].

<sup>6</sup> M. KLESSINGER, Fortschritte der Chemisechn Forschung, Bd. 9, Springer-Verlag, Berlin 1968, S. 419 ff.

<sup>7</sup> P. P. FEOFILOV, The Physical Basis of Polarised Emission, Consultants Bureau, New York 1961.

## Application of the PMO-Method to the Chemistry of Cyclopropane and Cyclobutane

MUTHANA SHANSHAL \*

Institut für Theoretische Chemie, Universität Stuttgart

(Z. Naturforsch. **27 a**, 1665—1671 [1972]; received 13 July 1972)

The chemistry of cyclopropane and cyclobutane may be treated in terms of a 2nd order PMO method similar to the treatment of even conjugated systems. Applied to several reactions of both molecules, the PMO method yields results in agreement with the available experimental and SCF-MO results. The present treatment removes the ambiguity about the conjugative and nonconjugative reactivities of both molecules. It constitutes another contribution toward a noncomputative theoretical chemistry.

The chemistry of conjugated molecules may be discussed in terms of a perturbation theory utilizing Hückel molecular orbitals as basis functions<sup>1</sup>. Dewar formulated this method, the Perturbation Molecular Orbital Method (PMO), and applied it for the study of a variety of substitution and addition reactions as well as for the prediction of relative stabilities of conjugated systems. This treatment was highly successful in deriving the general

Dewar-Evans rule of pericyclic reaction<sup>2</sup>, providing relative thermodynamic stabilities of possible transition states. Of particular interest is the work of DAUGHERTY<sup>3</sup> which showed that for certain photochemical reactions the concept of conservation of orbital symmetry<sup>4</sup> does not hold, whereas the PMO treatment does maintain its validity. The same author carried out recently a PMO treatment for mass-spectral reactions indicating its applicability

Reprint requests to Dr. M. SHANSHAL, Institut für Theoretische Chemie der Universität Stuttgart, D-7000 Stuttgart, Relenbergstraße 32.

\* Present address: Department of Chemistry, University of Bagdad, Bagdad, Irak.



Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition "no derivative works"). This is to allow reuse in the area of future scientific usage.

in this area. We have been applying this method for conformations in radicals, anions and nitrogen compounds and have been comparing the results with SCF-MO and experimental data<sup>5</sup>. In the following we describe an attempt for the extension of the PMO method to nonconjugated, smallring compounds.

We construct the ring molecular orbitals (MO's) from linear combinations of Walsh's p- and  $\sigma$ -atomic orbitals<sup>6</sup>. Further we neglect, in a first approximation, any interaction between the ( $\pi$ -) and ( $\sigma$ -) MO's. The ring MO's are constructed according to the Hückel method. It should be stressed that, although we use the Hückel MO's for our calculation, we don't apply the Hückel method itself for the prediction of the reactivity of the molecules. The PMO results are not necessarily similar to those of the Hückel theory. In fact both methods yield different sequences of stability for many conjugated molecules<sup>1</sup>.

For both ringsystems, cyclopropane and cyclobutane,

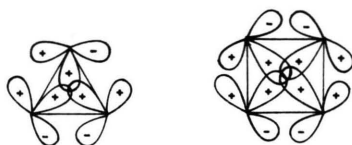


Fig. 1.

two sets of MO's are obtained,  $\sigma$  and  $\pi$ <sup>6a</sup>. For the three membered ring, the following eigenvalues and eigenvectors are calculated:

	$\sigma$ -MO's			$\pi$ -MO's		
	$\alpha+2\beta$	$\alpha-\beta$	$\alpha-\beta$	$\alpha+\beta$	$\alpha+\beta$	$\alpha-2\beta$
1	.58	.0	-.82	.0	-.82	.58
2	.58	.71	.41	.71	.41	.58
3	.58	-.71	.41	-.71	.41	.58

The occupation of the MO's is as follows:

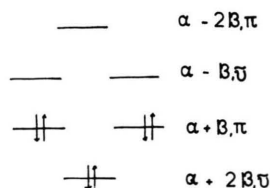


Fig. 2.

If we accept the approximation  $\beta_\sigma = \beta_\pi$  in our treatment, it follows that for the four membered ring the  $\sigma$ - and  $\pi$ -MO's are of the same pattern hav-

ing common values for the eigenvalues and eigenvectors. The calculated MO values are:

	$\alpha+2\beta$	$\alpha$	$\alpha$	$\alpha-2\beta$
1	.5	.5	.5	.5
2	.5	.5	-.5	-.5
3	.5	-.5	-.5	.5
4	.5	-.5	.5	-.5

As a result, a four fold degenerate MO level is obtained ( $2 \times \sigma$  and  $2 \times \pi$ ). To remove this degeneracy and allow for the singlett occupation of the orbitals, we introduce the  $\sigma-\pi$  interaction of the degenerate nonbonded MO's. The allowed combination is  $1/\sqrt{2} \cdot (\sigma_2 \pm \pi_2)$  and  $1/\sqrt{2} \cdot (\sigma_3 \pm \pi_3)$ . The energy levels for these MO's are as follows:

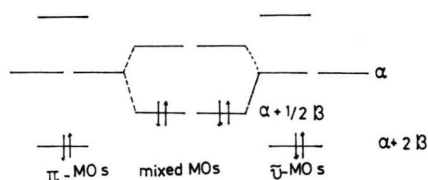


Fig. 3.

Other authors have made similar constructions for the MO's of both ring systems and found good qualitative agreement with the SCF-MO's<sup>7</sup>. Having constructed the necessary MO's of both ring systems we may carry out the PMO treatment for all their reactions. The following examples demonstrate the application of the method. Since in all these examples no degeneracy is to be found between the MO's of the ring and those of the reaction partner (except in that of vinylcyclopropane), only second order perturbation is significant for them<sup>1</sup>. This can be calculated using the following formulae:

$$\Delta E = 2 \left( \sum_{\mu}^{\text{occ.}} \sum_{\rho}^{\text{unocc.}} - \sum_{\rho}^{\text{occ.}} \sum_{\mu}^{\text{unocc.}} \right) \frac{a_{\mu r}^2 \cdot b_{\rho s}^2 \cdot \beta_{rs}^2}{E_{\mu} - E_{\rho}} \quad (1)$$

( $\Delta E$  = the change in energy due to reaction;  $\mu, \rho$  = MO's of the ring and the reaction partner;  $a_{\mu r}, b_{\rho s}$  = MO coefficients at atoms r and s where the reaction is taking place;  $\beta_{rs}$  = core resonance integral for the bond r-s;  $E_{\mu}, E_{\rho}$  = MO-energies of the ring and the reaction partner).

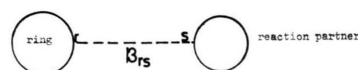


Fig. 4.

### The Protonation of Cyclopropane

Let us assume, for arithmetic convenience, that  $\alpha_H = \alpha_C$  and  $\beta_{C-H} = \beta_{C-C}$ . This assumption is justified since we are only interested in the relative stability of different protonation species rather than the absolute dimension of the protonation energies.

#### 1. Edge Protonation



Fig. 5 a.  
Interaction with the  
 $\sigma$ -MO's ( $\sigma$ -interaction)  
 $S \cong 0.0$ .

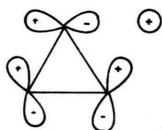


Fig. 5 b.  
Interaction with the  $\pi$ -MO's  
( $\pi$ -interaction).

$$\begin{aligned} \Delta E &= 2 \sum_{\mu}^{\text{occ.}} \frac{(a_{u,2} + a_{u,3})^2 \cdot \beta^2}{E_{\mu} - \alpha_H} + \frac{(a_{u,3} \cdot \beta_{3,H})^2}{E_u - \alpha_H} \\ &= 2 \left[ \frac{(0.+.71)^2 \beta^2}{\beta} + \frac{(.41 - .82)^2 \beta^2}{\beta} \right] \\ &= 1.34 \beta. \end{aligned}$$

The interaction between the  $H_{1s}$  orbital and the  $\sigma$ -MO's is negligible due to the large distance between their centers. The interaction with the  $\pi$ -MO's takes place on C-atoms 2 and 3. The second order perturbation energy is  $1.34 \beta$ .

#### 2. Corner Protonation

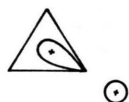


Fig. 6 a.  
 $\sigma$ -Interaction,  $S \cong 0.0$ .

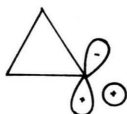


Fig. 6 b.  
 $\pi$ -Interaction,  $S = 0.0$ .

In this case, the interaction with the  $\sigma$ -MO's is negligibly small. The  $H_{1s}$  orbital attacks the C atom from the side of its small negative lobe. As for the  $\pi$ -MO's, no interaction takes place either; the overlap between the  $H_{1s}$  orbital and the adjacent p-atomic orbital is nil for symmetry reasons.

#### 3. Face Protonation



Fig. 7 a.  $\sigma$ -Interaction  
 $\Delta E = 2 \left[ \frac{(3 \times .58 \beta)^2}{2 \beta} \right] = 3.0 \beta.$



Fig. 7 b.  
 $\pi$ -Interaction,  $S = 0.0$ .

The  $\sigma$ -interaction proceeds with all  $\sigma$ -lobes participating in the formation of the occupied  $(\alpha + 2 \beta)$   $\sigma$ -MO. The  $\pi$ -interaction is nil, for the  $H_{1s}$  orbital interacts equally with both lobes of each p-atomic orbital (p-AO). The face protonation becomes less favourable on regarding the repulsion energy of the proton with the three neighboured hydrogenatoms ( $\sim 2.8 \beta$  estimated according to Bartell's function<sup>18</sup>). The net bonding energy amounts  $0.2 \beta$ .

Our treatment shows that the protonation of cyclopropane should proceed on an edge rather than a corner or a face of the cyclic system. This result is in qualitative agreement with recent SCF-MO calculations<sup>8</sup> and experimental data<sup>9</sup> yielding the stability of the edge protonated form.

A rather interesting conclusion may be drawn from the discussion of OLAH's recent work<sup>10</sup> in the light of the present treatment. It was found for the norbornyl carbonium ion that an NMR line splitting at low temperature, corresponding to an activation energy of 5.9 kcal/mole, could be attributed to the 6,1,2 hydrogenshift in the cyclic 3 membered face of the ion. Further, the corner protonated non-classical structure of the molecule was assumed. The assumed structure was then:

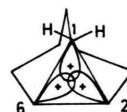


Fig. 8. Olah's structure for the norbornyl cation.

At first glance, this result seems to contradict our present conclusion. However, it is easily seen that a corner protonation is by no means compatible with the Walsh's description of the bonding in the 3 membered ring. It is not even in agreement with the concept of maximum overlap determining the bondstrength. A corner protonation demands the rehybridization of the corresponding C atom. This proceeds at the expense of Walsh's  $\sigma$ -AO and results in its complete disappearance in the extreme case of covalent  $-CH_2$  binding.

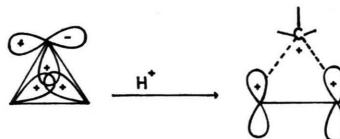


Fig. 9.

Corner protonation

In other words, corner protonation should cause the explosion of the 3 membered ring in olefine and  $R-CH_2^+$  fragments. It is rather logical that the compound studied by Olah was a  $\pi$ -complex undergoing rapid hydrogen shift accompanied by skeletal rearrangement. In fact, Dewar suggested many years ago that the discussion about the classical or non-classical structure of these ions is irrelevant; the ions resembling charged  $\pi$ -complexes<sup>1</sup>. Certainly, Olah's measurement is in agreement with Dewar's assumption and with our present analysis.

However, whereas the charged  $\pi$ -complex may be stabilized through interaction with the adjacent paraffinic chain of the norbornyl cation, there is no way of stabilizing such a complex in the cyclopropane molecule itself. The only possible mode of protonation left for this molecule then is the edge protonation. We may conclude that the reactivity of both carbonium ions is not totally similar and analogies should not necessarily be drawn from the chemistry of one to that of the other<sup>10, 11</sup>.

### Conformation of the Cyclopropyl-carbinyl Cation

#### 1. The Bisected Form

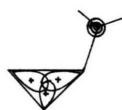


Fig. 10 a.  
 $\sigma$ -Interaction,  $S=0.0$ .

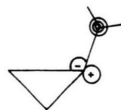


Fig. 10 b.  $\pi$ -Interaction;

$$\Delta E = 2 \times \left[ \frac{(.41\beta)^2}{\beta} + \frac{(.71\beta)^2}{\beta} \right] = 1.34\beta$$

The interaction of the empty p-atomic orbital of the methylene group with the adjacent  $\sigma$ -orbital is nil due to symmetry. Its interaction with the neighbored p-AO is of the magnitude  $1.34\beta$ . The total interaction energy with both doubly occupied  $\pi$ -MO's is  $1.34\beta$ .

#### 2. The Planar Form

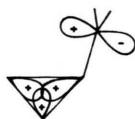


Fig. 11 a.  $\sigma$ -Interaction.

$$E = 2 \times \frac{(.58\beta)^2}{2\beta} = .34\beta.$$

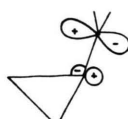


Fig. 11 b.  
 $\pi$ -Interaction,  $S=0.0$ .

The  $\sigma$ -interaction compells the conjugation of the empty methylene lone orbital with the  $\sigma$ -MO's of the ring. The corresponding interaction energy is  $.34\beta$ . The interaction with the  $\pi$ -MO's is nil due to the orthogonality of the empty lone orbital and the adjacent p-AO. The energy difference for both structure is,

$\Delta E^\ddagger(\text{bisected-planar}) = 1.34\beta - .34\beta = 1.00\beta$ , indicating the relative stability of the bisected over the planar form. The rotation barrier

$$\Delta E^\ddagger = 1.0\beta \cong 18 \text{ kcal/mol}$$

is of remarkable agreement with recent SCF-MO<sup>12</sup> (16 kcal/mol) and NMR-results (13.9 kcal/mol)<sup>13</sup>.

### The Conformation of Vinyl-cyclopropane

For this molecule we consider only the interaction of the ethylenic  $\pi$ -MO's with the MO's of the ring. Due to the doubly occupation of all the interacting bonding orbitals, no first order perturbation shall be considered.

#### 1. The Planar Conformation

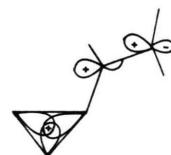


Fig. 12 a.  
 $\sigma$ -Interaction

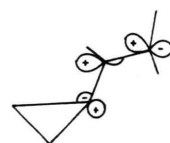


Fig. 12 b.  
 $\pi$ -Interaction;  $S=0.0$

$$\Delta E = 2 \left[ \frac{(.58 \cdot 1/\sqrt{2} \cdot \beta)^2}{\alpha + 2\beta - \alpha + \beta} + \frac{(1/\sqrt{2} \cdot 0 \cdot \beta)^2}{\alpha + \beta - \alpha + \beta} + \frac{(1/\sqrt{2} \cdot .82 \cdot \beta)^2}{\alpha + \beta - \alpha + \beta} \right] = .45\beta.$$

The  $\sigma$ -interaction yields an increase in bonding energy of  $.45\beta$ . The  $\pi$ -interaction is nil because of the orthogonality of both  $\pi$ -systems.

#### 2. The Bisected Conformation

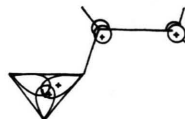


Fig. 13 a.  
 $\sigma$ -Interaction;  $S=0.0$

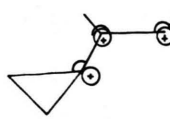


Fig. 13 b.  
 $\pi$ -Interaction

$$\Delta E = 2 \left[ \frac{[.82 \cdot (1/\sqrt{2}) \cdot \beta]^2}{\alpha + \beta - \alpha + \beta} + 9 + \frac{[(1/\sqrt{2}) \cdot .58 \cdot \beta]^2}{\alpha + \beta - \alpha + \beta} \right] = .45\beta.$$

The interaction with the  $\sigma$ -MO's is nil due to symmetry. The  $\pi$ -interaction amounts to  $.45\beta$ .

The PMO-treatment yields no barrier, or a very small one, for the rotation of the vinyl group around its bond axis to the cyclopropane ring. The measured NMR barrier is  $< 1.00$  kcal/mol<sup>14</sup>.

### The Protonation of Cyclobutane

We will consider the mixed MO's of cyclobutane,  $(1/\sqrt{2}) \times (\sigma_2 \pm \pi_2)$  and  $(1/\sqrt{2}) \times (\sigma_3 \pm \pi_3)$  by both  $\sigma$ - and  $\pi$ -perturbations. Their MO coefficients at the corresponding atom of interaction are obtained by multiplying the original MO coefficients with  $1/\sqrt{2}$ .

#### 1. The Edge Protonation

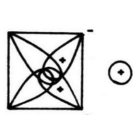


Fig. 14 a.  
 $\sigma$ -Interaction;  $S=0.0$

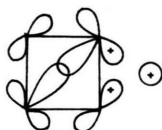


Fig. 14 b.  
 $\pi$ -Interaction

$$\Delta E = 2 \left[ \frac{(2 \times .5 \beta)^2}{2 \beta} + \frac{(2 \times .5 \times \beta)^2 \cdot .5 + 0}{.5 \beta} \right] = 3.0 \beta$$

The  $\sigma$ -interaction is negligibly small. The  $\pi$ -interaction occurs with 2 adjacent atoms. Considering the coefficients of the new mixed MO's and approximating  $\beta_\sigma \cong \beta_\pi$ , we obtain the interaction energy  $3.0 \beta$  for the edge protonation.

#### 2. The Corner Protonation

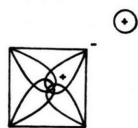


Fig. 15 a.  
 $\sigma$ -Interaction;  $S \cong 0.0$

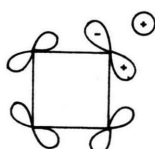


Fig. 15 b.  
 $\pi$ -Interaction;  $S=0.0$

Both interactions vanish. The  $\sigma$ -interaction is quite negligible, the  $\pi$ -interaction vanishes through symmetry.

#### 3. The Face Protonation

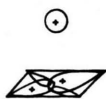


Fig. 16 a.  
 $\sigma$ -Interaction,

$$\Delta E = 2 \left[ \frac{(4 \times .5 \beta)^2}{2 \beta} + 0 \right] = 4 \beta$$

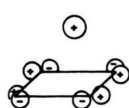


Fig. 16 b.  
 $\pi$ -Interaction;  $S=0.0$

Since the empty  $H_{1s}$  orbital interacts equally with both lobes of each p-orbital, the total  $\pi$ -interaction is nil. The  $\sigma$ -interaction is positive and amounts  $4.0 \beta$ . A rough estimation of the repulsion energy between the proton and the four neighbored hydrogenatoms, using the Bartell's function, yielded 22 kcal/mol ( $\sim 1.2 \beta$ ). The net binding energy is then  $2.8 \beta$ . Our treatment indicates that the face and edge protonated cyclobutanes are almost equally stable, and that the latter is slightly more stable than the first (energy difference =  $.2 \beta$ ).

### The Conformation of Cyclobutylcarbinyl Cation

In a similar manner to the treatment of the cyclopropylcarbinyl cation, the interaction of the empty lone orbital with the  $\sigma$ - and  $\pi$ -MO's of the ring can be treated on the basis of 2-nd order PMO method.

#### 1. The Bisected Conformation



Fig. 17 a.  
 $\sigma$ -Interaction;  $S=0.0$

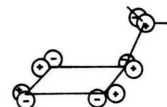


Fig. 17 b.  
 $\pi$ -Interaction,

$$\Delta E = 2 \left[ \frac{(.5 \beta)^2}{2 \beta} + 2 \times \frac{(1/\sqrt{2} \cdot .5 \beta)^2}{1/\sqrt{2} \cdot \beta} \right] = 1.25 \beta$$

The  $\sigma$ -interaction vanishes because of the anti-symmetric interaction of both lobes of the lone orbital with the adjacent  $\sigma$ -atomic orbital. The  $\pi$ -interaction amounts to  $1.25 \beta$ .

#### 2. The Planar Conformation



Fig. 18 a.  
 $\sigma$ -Interaction;

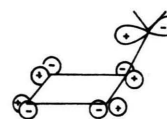


Fig. 18 b.  
 $\pi$ -Interaction;  $S=0.0$

$$\Delta E = 2 \left[ \frac{(.5 \beta)^2}{2 \beta} + 2 \times \frac{2 \times (1/\sqrt{2} \cdot .5 \beta)^2}{\frac{1}{2} \beta} \right] = 1.25 \beta$$

The  $\sigma$ -interaction of the lone orbital yields a (conjugation) energy  $1.25 \beta$ . The  $\pi$ -interaction is nil, since the lone orbital interacts equally with both lobes of the adjacent p-AO.

The PMO treatment for the cyclobutylcarbinyl cation yields no barrier for the rotation of the methylene group around its bond axis. Both confor-

mations are equally conjugated with the ring. In fact, SCF-MO calculations yielded only small values for the rotation barrier of the same system<sup>15</sup>. Our treatment indicates too that the nonexistence of the barrier is not due to lack of conjugation, but rather due to the equal conjugation of this orbital with both  $\pi$ - and  $\sigma$ -MO systems of the ring.

### The Conformation of Vinylcyclobutane

The interaction of both segments, ethylene and cyclobutane, differs from the interactions in the two previous cyclobutane systems in that both segments possess occupied orbitals. We consider only the interaction of the ring MO's with the  $\pi$ -MO's of the ethylene segment, whose MO coefficients are;

$$\begin{aligned}\varepsilon = \alpha + \beta & \quad 1/\sqrt{2} \quad 1/\sqrt{2} \\ \varepsilon = \alpha - \beta & \quad 1/\sqrt{2} \quad -1/\sqrt{2}\end{aligned}$$

Further we apply the following equation for the calculation of interaction energies<sup>1</sup>;

$$\Delta E = 4 \sum_{\mu}^{\text{occ}} \sum_{\nu}^{\text{dec}} \frac{(a_{\mu r} \cdot b_{\nu s} \cdot \beta_{rs})^2}{E_{\mu} + E_{\nu}} \quad (2)$$

Equation (2) is a direct result of introducing Coulson's Pairing Theorem to Equation (1).

#### 1. The Bisected Form

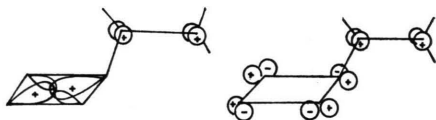


Fig. 19 a.  
 $\sigma$ -Interaction;  $S=0.0$

Fig. 19 b.  
 $\pi$ -Interaction;

$$\Delta E = 4 \left[ \frac{[.5 \cdot (1/\sqrt{2}) \cdot \beta]^2}{\alpha + 2\beta + \alpha + \beta} + \frac{2 \times (.5 \cdot \frac{1}{2} \beta)^2}{\alpha + \frac{1}{2}\beta + \alpha + \beta} \right] = .5\beta.$$

The  $\sigma$ -interaction vanishes due to symmetry. The  $\pi$ -interaction yields an increase in the conjugation energy of  $.5\beta$ .

#### 2. The Planar Form

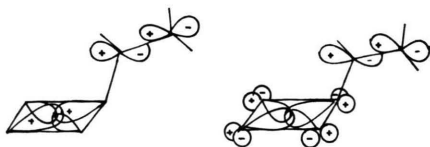


Fig. 20 a.  
 $\sigma$ -Interaction;

Fig. 20 b.  
 $\pi$ -Interaction;  $S=0.0$

$$\Delta E = 4 \left[ \frac{[.5 \cdot (1/\sqrt{2}) \cdot \beta]^2}{\alpha + 2\beta + \alpha + \beta} + \frac{2 \times (.5 \cdot \frac{1}{2} \beta)^2}{\alpha + \frac{1}{2}\beta + \alpha + \beta} \right] = .5\beta.$$

The  $\sigma$ -interaction yields a conjugation energy  $.5\beta$ , the  $\pi$ -interaction is nil.

The predicted rotation barrier for the ethylene segment around its bond axis is nil also. This is due to equal conjugation of the ethylenic group to the  $\sigma$ - and  $\pi$ -MO's in the two conformations. It may be pointed out, that the actual barrier need not necessarily be 0.0 kcal/mol; for other factors such as nonbonded repulsion or the fact that  $\beta_{\sigma}$  not exactly equals  $\beta_{\pi}$  may influence the barrier height. The rotation barrier should however be small (smaller than that for cyclopropylcarbinyl cation).

### Appendix

#### The Construction of the Cyclobutyl Degenerate MO's

The combination of a  $\sigma_2$  and a  $\pi_3$  type MO's results in no removal of degeneracy. This can be found by investigation of the above MO coefficients. Only combination of the type  $(1/\sqrt{2}) \times (\sigma_2 \pm \pi_2)$  or  $(1/\sqrt{2}) \times (\sigma_3 \pm \pi_3)$  can remove the degeneracy. The energy of the new MO's are;

$$\begin{aligned}\varepsilon &= \frac{1}{2} \int (\sigma_3 \pm \pi_3) \mathbf{H} (\sigma_3 \pm \pi_3) d\tau \\ &= \frac{1}{2} (H_{\sigma_3\sigma_3} + H_{\pi_3\pi_3} + H_{\sigma_1p_1} \mp H_{\sigma_1p_2} + H_{\sigma_1p_3} \mp H_{\sigma_1p_4} \\ &\quad \mp H_{\sigma_2p_1} + H_{\sigma_2p_2} \mp H_{\sigma_2p_3} + H_{\sigma_2p_4} + H_{\sigma_3p_1} \mp H_{\sigma_3p_2} + H_{\sigma_3p_3} \\ &\quad \mp H_{\sigma_3p_4} \mp H_{\sigma_4p_1} + H_{\sigma_4p_2} \mp H_{\sigma_4p_3} + H_{\sigma_4p_4}) \quad (3) \\ q_n &= sp^2\text{-hybridized atomic orbital;} \\ p_n &= p\text{-atomic orbital.}\end{aligned}$$

The values for  $H_{\sigma\sigma}$  and  $H_{\pi\pi}$  are  $\alpha$  and  $\alpha$  respectively. All the other expectation values, except those with double signs, vanish through symmetry.

$$\begin{aligned}\varepsilon &= \alpha \mp .25(\beta_{12} + \beta_{14} + \beta_{21} + \beta_{23} + \beta_{32} + \beta_{34} + \beta_{41} + \beta_{43}) \\ &= \alpha \mp 2\beta_{\sigma-\pi}.\end{aligned} \quad (4)$$

Since our whole treatment has been of approximate nature, we have no other choice than to estimate the value of the  $\beta_{\sigma-\pi}$  core resonance integral approximately. We first accept the following relation;

$$\beta_{ij} \propto S_{ij} \propto (1/r_{ij}) \quad (5)$$

and then set  $r_{ij}$  equal to the distance between the centers of gravity of the two orbitals ( $i$  and  $j$ ).

$$r_{ij} = \langle i | \mathbf{r} | i \rangle - \langle j | \mathbf{r} | j \rangle. \quad (6)$$

The expectation value  $\langle i | \mathbf{r} | i \rangle$  may be calculated according to the following formulae<sup>16</sup>;

$$\bar{r} = \langle i | \mathbf{r} | i \rangle = \frac{n^2 \cdot a_0}{Z} \left[ 1 + \frac{1}{2} \left\{ 1 - \frac{l(l+1)}{n^2} \right\} \right]. \quad (7)$$

For a single lobe in a 2p-AO one obtains  $\bar{r} = .44 \text{ \AA}$ . For an  $sp^2$ -Orbital we calculate;

$$\langle \sqrt{\frac{1}{3}} S + \sqrt{\frac{2}{3}} P | \mathbf{r} | \sqrt{\frac{1}{3}} S + \sqrt{\frac{2}{3}} P \rangle \quad (8)$$

$$= \frac{1}{3} \langle S | \mathbf{r} | S \rangle + 2 \times \frac{2}{3} \langle S | \mathbf{r} | P \rangle + \frac{2}{3} \langle P | \mathbf{r} | P \rangle \cong \frac{1}{2} \bar{r}_P.$$

Since each  $sp^2$ -AO overlaps differently with both lobes of each neighbored p-AO, its distance to them ( $R^+$  and  $R^-$ ) should be estimated.

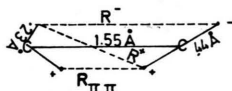


Fig. 21.

Given that the C-C bondlength is  $1.55 \text{ \AA}$ , one can calculate both distances as well as the  $R_{\pi\pi}$  dis-

tance. The obtained values are

$$R^- = 1.66 \text{ \AA}, \quad R^+ = 1.16 \text{ \AA} \quad \text{and} \quad R_{\pi\pi} = .93 \text{ \AA}.$$

It follows then that;

$$S_{\sigma-\pi} : S_{\pi-\pi} = R_{\pi\pi}/R^+ - R_{\pi\pi}/R^-$$

$$= \beta_{\sigma-\pi} : \beta_{\pi\pi} = .25 \quad (9)$$

and that  $\beta_{\sigma\pi} = .25 \beta_{\pi\pi}$ . The orbital energies of the new mixed and doubly degenerate MO's are then  $\epsilon = \alpha \mp .5 \beta$ .

#### Acknowledgement

I thank Prof. H. PREUSS for providing the research possibility at the above mentioned institute, Mr. P. COFFEY for the correction of the text and the Deutsche Forschungsgemeinschaft for financial support.

\*\* On preparing this manuscript we became aware of several works, which appeared recently, discussing the structure of the protonated cyclopropane. Applying the MINDO/2 method DEWAR and BODOR found, in agreement with our PMO treatment, that the edge protonated species is the more stable<sup>17</sup>. Contrary to this result, POPLE and co-workers<sup>18</sup>, applying the 4G-STO method, came to the conclusion that the corner protonated species is the more stable one. Both calculations for the corner protonated species yielded an elongation in the  $\text{CH}_3^+ \dots \text{CH}_2$  bond, which corresponds to the formation of a  $\pi$ -complex. Pople's calculation yielded a bondlength of  $\sim 3.4 \text{ at. u.}$  Such an elongation of bond causes normally a nonnegligible change in correlation energy. Added to this is the fact that edge and corner protonated species correspond to different symmetries, a factor which influences the in-out and angular correlation energies, which are inherent in ab initio methods. Since there had been no CI treatment done for this problem, one cannot feel confident about this result. It should be mentioned that the 4G-STO method does not supply apply a complete basis set and the calculations done with it are not near the Hartree-Fock limit. — OLAH et al. published an ESCA measurement of the protonated norbornyl system<sup>19</sup>. The results are conclusively not different from his previous CMR results<sup>10</sup> and certainly not definitely conclusive for this problem of cyclopropane's protonation (edge-, corner-protonation or a  $\pi$ -complex formation). The detection of two C-signals with the integration ratio 2 : 5 may well be explained through the existence of an edge protonated species.

<sup>1</sup> M. J. S. DEWAR, *The Molecular Orbital Theory of Organic Chemistry*, McGraw-Hill Book Co., New York 1969.

<sup>2</sup> M. J. S. DEWAR, *Tetrahedron Supplement* **8**, 75 [1966]; *Angew. Chem. intern. Edit.* **10**, 761 [1971].

<sup>3</sup> R. DAUGHERTY, *J. Amer. Chem. Soc.* **93**, 7187 [1972].

<sup>4</sup> H. C. LONGUET-HIGGINS and E. W. ABRAHAMSON, *J. Amer. Chem. Soc.* **87**, 2045 [1965]. — R. B. WOODWARD and R. HOFFMANN, *Angew. Chem.* **81**, 797 [1969].

<sup>5</sup> M. SHANSHAL, *Z. Naturforsch.* **25b**, 1063, 1065 [1970]; *Theor. Chim. Acta* **21**, 149 [1971]; *Tetrahedron* **28**, 61 [1972].

<sup>6</sup> A. D. WALSH, *Nature London* **159**, 167, 712 [1947]; *Trans. Faraday Soc.* **45**, 179 [1949].

<sup>6a</sup> The term ( $\pi^-$ ) should not be related here to the magnitude of the total angular momentum of the MO. It identifies this orbital as composed of p-AO's only.

<sup>7</sup> For references see R. HOFFMANN and R. B. DAVIDSON, *J. Amer. Chem. Soc.* **93**, 5699 [1971].

<sup>8</sup> R. SUSTMAN, J. E. WILLIAMS, M. J. S. DEWAR, L. C. ALLEN, and P. v. R. SCHLEYER, *J. Amer. Chem. Soc.* **91**, 5350 [1969].

<sup>9</sup> R. L. BAIRD and A. A. ABODERIN, *J. Chem. Soc.* **86**, 252 [1964]. — N. C. DENO, D. LA VIETES, J. MOCKUS, and P. C. SCHOLL, *J. Amer. Chem. Soc.* **90**, 6457 [1968]. — C. J. COLLINS, *Chem. Rev.* **69**, 541 [1969].

<sup>10</sup> G. A. OLAH, A. M. WHITE, J. R. DEMEMBER, A. COMMEYRAS, and C. Y. LUI, *J. Amer. Chem. Soc.* **92**, 4627 [1970].

<sup>11</sup> G. KLOPMAN, *J. Amer. Chem. Soc.* **91**, 89 [1969]. — The available SCF-MO results attribute a significant stability of the corner relative to the face protonation in contradiction to our treatment. This deviation may be attributed to the nonbonded repulsion between the proton and the three ringhydrogen atoms facing it. Our PMO treatment does not consider such interaction.

<sup>12</sup> M. SHANSHAL, *Theoret. Chim. Acta* **20**, 405 [1971].

<sup>13</sup> D. S. KABAKOFF and E. NAMANWORTH, *J. Amer. Chem. Soc.* **92**, 3234 [1970].

<sup>14</sup> W. LUTTKE and A. DE MEIJERE, *Angew. Chem.* **78**, 544 [1966]. — H. GUNTHER and D. WENDISCH, *Angew. Chem.* **78**, 266 [1966]. — G. R. DE MARE and J. S. MARTIN, *J. Amer. Chem. Soc.* **88**, 5033 [1966].

<sup>15</sup> L. RADOM, J. A. POPLE, V. BUSS, and P. v. R. SCHLEYER, *J. Amer. Chem. Soc.* **92**, 6380 [1970].

<sup>16</sup> L. PAULING and E. B. WILSON, *Introduction to Quantum Mechanics*, McGraw-Hill Book Co., Inc., New York 1935, p. 144.

<sup>17</sup> M. J. S. DEWAR and N. BODOR, *J. Amer. Chem. Soc.* **93**, 6685 [1971].

<sup>18</sup> L. RADOM, J. A. POPLE, V. BUSS, and P. v. R. SCHLEYER, *J. Amer. Chem. Soc.* **94**, 311 [1972]. — L. S. BARTELL, *J. Chem. Phys.* **32**, 827 [1960].

<sup>19</sup> G. A. OLAH, G. D. MATESCU, and J. L. RIEMENSCHNEIDFR, *J. Amer. Chem. Soc.* **94**, 2530 [1972].