

Ab Initio Study of Stability and Strain of Cyclopropane and Its Derivatives

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The peculiar properties of the three-membered ring (C_3 ring) in cyclopropane and its derivatives are due to characteristic bonding and electronic effects. Contraction of the atomic orbitals (AO's) composing the C–C bonding molecular orbitals (MO's) of a_1 symmetry favors stability of the C_3 ring. Expansion of the e' HOMO AO's contributes to the formation of peripheral "pseudo- π bonds". The stability of the C_3 ring also correlates with substitution of the ring.

INTRODUCTION

Ab initio MO calculations have been performed and analyzed on propane (P), cyclopropane (CP), vinylcyclopropane (VCP) and cyclopropanecarbaldehyde (CPCA) using the Dunning basis set at optimized geometries. Electronic effects and bond orbitals on the ring are analyzed from the results of these calculations.

The bond energies of the C_3 ring skeletons can be obtained by subtraction of the atomization energies of CP or P from the standard C–H bond energy.¹ The additional stabilization of about 2.4 eV in CP, which is thermally stable, has been interpreted by Dewar³ as being due to σ -conjugation of the three C–C bonds leading to aromaticity. Epiotis³ has suggested superaromatic interaction between the cyclic C–C bonds and the C–H bonds. Cremer⁴ attributed the stabilization to surface delocalization of electrons over the plane of the ring.

There are two models that could serve to rationalize these facts. The Forster–Moffitt model⁵ postulates that three equivalent, localized, bent two-center σ -bonds are formed by $C(2sp^5)$ -hybridized AO's. Walsh's model⁶ requires a stable central three-center bond of a_1 symmetry, formed by inwardly directed sp^2 AO's, and two weak peripheral three-center bonds (p_r-e_x , p_r-e_y) of e symmetry formed by the tangential in plane $C(2p_t)$ AO, i.e., pAO's of the CH_2 portion.

The C_3 ring is thermochemically destabilized and easily undergoes ring opening in chemical reactions. The ring contains extremely small bond angles and is considerably strained, and it is widely believed that stability is related primarily to molecular strain, i.e., the more strain, the less stability and the less strain, the more stability. Dill et al.⁶ studied electronic and substituent effects in a series of the C_3 ring derivatives and concluded that if the stability of the C_3 ring is increased by the influence of substituents, the strain energy will be decreased. Cremer and Kraka⁴ analyzed the influence of substituents upon adjacent carbon atoms in the C_3 ring according to the relationship between σ -aromaticity and strain energy formulated by Dewar,² and suggested that σ -aromaticity of the C_3 ring is increased by electron-donating substituents and that the strain energy is also increased. This paper examines some new aspects of C_3 ring system stability and strain energy derived from *ab initio* calculations.

METHODS AND RESULTS

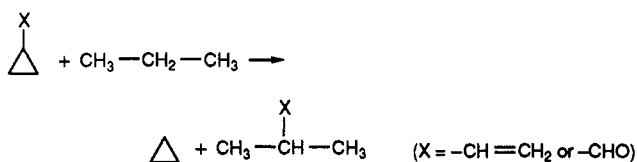
Using the Gaussian-80 program on a FACO-340 computer and 3-21G basis functions optimizing VCP and CPCA geometries, one can determine the details of the VCP and

CPCA stable *trans*-structure (Figure 1 and Table 1). *Ab initio* calculations on VCP and CPCA have been performed with these structures, using LCAO-MO-HFR-SCF method with Dunning basis functions (9s5p/4s2p)⁷. The results of these calculations are the total energy of the molecule and the energies of the different molecular orbitals, along with a characteristic vector (two irreducible representations a' and a'' on the XZ symmetrical plane of VCP and CPCA), the electron densities of different orbitals, and the total electron density isograms depicted in Figures 2 and 3.

DISCUSSION

Deformation of the C_3 Ring. The length (R_a) of the two C–C bonds adjacent to the substituent are longer in comparison to the bond lengths of the original compound CP, and the C–C bond length (R_o) opposite the substituent becomes shorter (Table 1). Thus the R_o bond center electron density becomes higher. In general, bond center electron density is an important mark of bond strength and ring stability. However as is clear from Walsh's model,⁶ the dominant factor deciding stability is the central electron density of the C_3 ring. Figure 2 clearly shows that the central electron density of VCP is decreased as compared to CP and, conversely, the central electron density of CPCA is increased. As a consequence, the stability of VCP is decreased and, in contrast, that of CPCA is increased.

Strain Energy of the C_3 Ring. Thermodynamic evaluation of the system shows that the calculated strain energies⁹ of



VCP and CPCA respectively are 10.2 and 14.0 kJ·mol⁻¹ lower than in CP. Thus, conclusion is not consistent with the above discussion, and suggests there may be some other relationship between stability and strain energy in the C_3 ring.

Orbital Analysis of the C_3 Ring. Orbital figures of CP, VCP, and CPCA are presented in Figure 3. The stabilization of the C_3 ring corresponds to high central bond charge of $2a_1'$ and $3a_1'$ orbitals in CP. Walsh's a_1' MO's are σ orbitals, which, due to AO contraction, have lower potential energies, whereas Walsh's e' MO's are π orbitals, which often show slight orbital expansion. The potential energies (in hartrees) of e' orbital and a_1' orbitals are -1.63 (higher), and -1.11 (lower), respectively, in CP⁵, indicating expansion of the AO's in CP.

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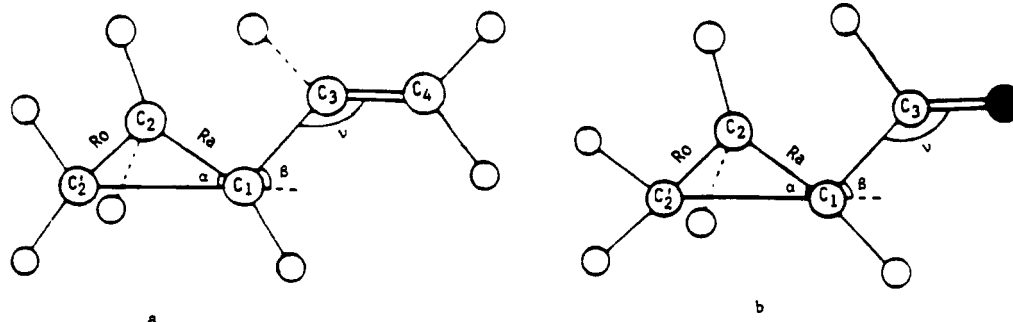


Figure 1. Molecular structure of VCP (a) and CPCA(b) (where O is H, R_0 , R_a are bond lengths, α , β , γ are bond angles).

Table 1. Bond Length ($\times 10^{-1}$ nm) and Bond Angle (deg) of CP, VCP, CPCA

molecule	method	C_1-C_2	C_2-C_2'	C_1-C_3	$C=C$	$C=O$	α	β	γ
CP	optimized value	1.512	1.512				60		
	ED value ⁸	1.510	1.510						
VCP	optimized value	1.519	1.510	1.477	1.317		59.48	56.70	125.30
	ED value ⁸	1.522	1.522	1.475					
CPCA	optimized value	1.521	1.499	1.472		1.209	59.04	59.20	125.40

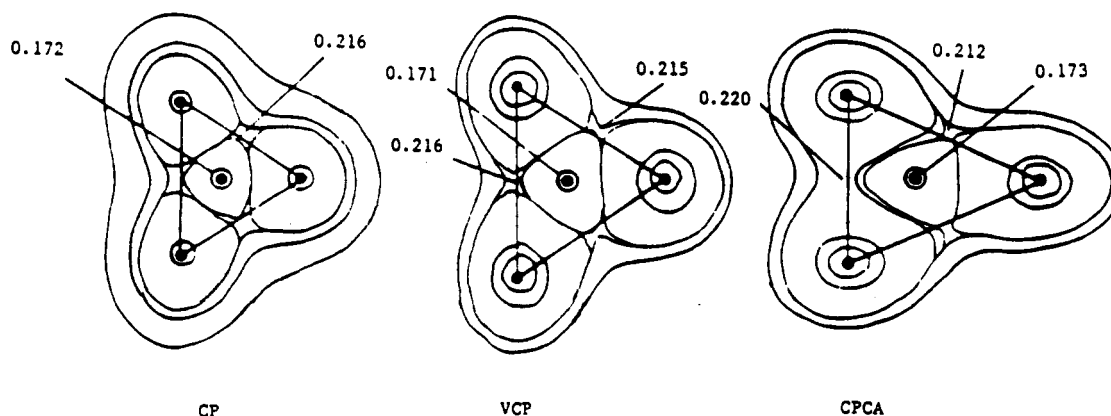


Figure 2. Electron density isogram (in XY plane of C_3 ring).

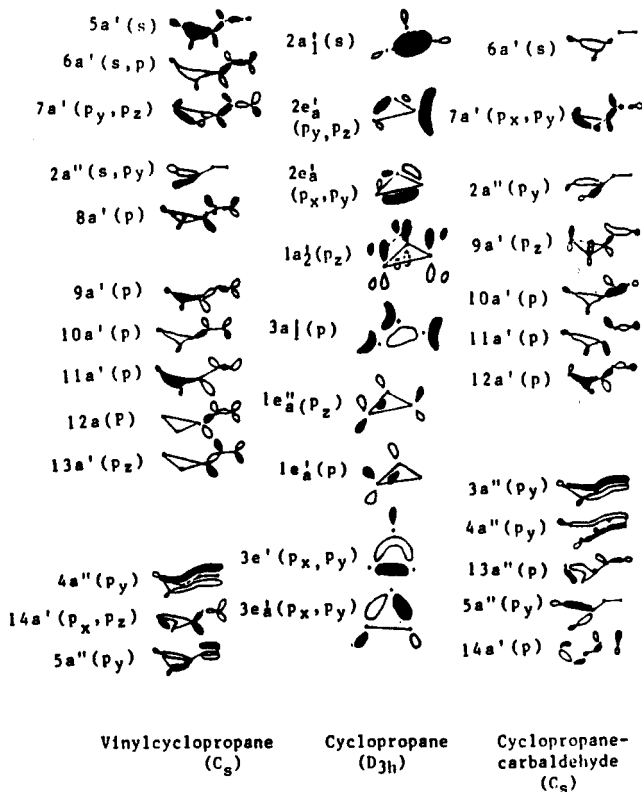


Figure 3. Bonding orbital comparison of CP, VCP, and CPCA.

Influence of Substituents $-\text{CH}=\text{CH}_2$ and $-\text{CHO}$ on MO's of the a' Type of the C_3 Ring. Orbitals $5a'$, $6a'$, $9a'$, $10a'$, and $11a'$ in VCP and $6a'$, $10a'$, $11a'$, and $12a'$ in CPCA correspond to $2a'$ and $3a'$ in CP. We note that the central three-center-bond charges transferred toward the base (C_2-C_2') of the C_3 ring through the σ -electron-donating effect of $-\text{CH}=\text{CH}_2$ and $-\text{CHO}$ and the order of the electron densities in the three-center bond is as follows (see Table 2):

$$\text{CP} (0.172) > \text{CPCA} (0.165) > \text{VCP} (0.157)$$

Response of the three-center-bond charges to the base of the C_3 ring is considered to weaken the stability and an electron donor is an important feature which can affect the ring stability.

Influence of Substituents $-\text{CH}=\text{CH}_2$ and $-\text{CHO}$ on e' Type MO's of the C_3 Ring. The "pseudo- π bond" ($3e_a'$) in CP and the P_y orbitals of $-\text{CH}=\text{CH}_2$ or $-\text{CHO}$ form a conjugated system ($4a''$ in VCP, $3a''$, $4a''$ in CPCA), in which π -electrons "flow" toward the substituents as a result of the π -electron-withdrawing effect of $-\text{CH}=\text{CH}_2$ and $-\text{CHO}$. This leads to a lowering of the bond electron density (Table 3). As to electron-withdrawing effects of $-\text{CH}=\text{CH}_2$ and $-\text{CHO}$, Dill has suggested that although the C_1-C_2' bond electron density is decreased, charge is transferred from σ -HOMO (highest occupied MO) to σ -LOMO (lowest occupied MO) through a σ -type orbital inductive effect. The effect of this on the ring charge is that electrons "flow" from the " σ -type orbital" with higher energy to a " σ -type orbital" with lower energy, resulting in decreased ring energy and increased ring stability. Con-

Table 2. Maximum Electron Density of Three-Center Bond in Molecular Center

orbitals	5a'	6a'	9a'	10a'	11a'	12a'	total
VCP	0.082	0.008	0.015	0.032	0.020		0.057
CPCA		0.090		0.058	0.016	0.001	0.165
CP		0.096 (2a ₁ ')	0.076 (3a ₁ ')				0.172

Table 3. Maximum Center Electron Density of C₁-C₂ (or C₁-C₃) Bond

	CP	VCP	CPCA
MO	3e _a ' (0.076)	4a'' (0.44, π) 5a'' (0.027)	3a'' (0.004, π) 4a'' (0.005, π) 5a'' (0.057)
D _{tot}	0.076	0.072	0.057

sequently, the stability of the C₃ ring with substituents depends on the relative strength of σ -electron-donating and π -electron-withdrawing effects of the substituents. For example, σ -donating > π -accepting for -CH=CH₂ in VCP, but σ -donating < π -accepting for -CHO in CPCA and, as a result, CPCA is more stable than VCP.

Mulliken population analysis on CPCA suggests that -CHO is the stronger electron-withdrawing group. Moreover, π -accepting > σ -donating. This is consistent with the above MO calculation.

Strain Energy of the C₃ Ring. According to the definition of strain energy, if the C₃ ring energy decreases, the strain energy should decrease. In other words, strain energy depends only on the π -electron effect of the substituents in which electrons are transferred from HOMO to LOMO. This differs from Dewar's formulation in which σ -aromaticity is always concerned with strain energy. Dill and Cremer also suggest that σ -electron-donating groups can increase the stability of the C₃ ring.

CONCLUSION

As discussed above, -CH=CH₂ and -CHO were chosen as two typical substituents to determine whether σ -electronic effects or π -electronic effects have the greater effect on the stability of the C₃ ring. This study finds that σ -donation results in decreased stability and the π -electron-withdrawing effect results in increased stability. Thus the overall stability is a combination of both these effects. Strain energy change only depends on the π -electron effect of substituents in which an electron is transferred between HOMO and LOMO. A π -electron-withdrawing group leads to decreased strain energy.

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