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Electronic Structures and Reactivities of Aliphatic Small-Membered-Ring Compounds. I[*1]

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Extended LCAO MO investigations into the physico-chemical properties of cycloalkanes and their derivatives are carried out. The bond natures of C–C and C–H in cycloalkanes, the electronic distributions of the lowest vacant orbital, the electron-attracting powers of the ring, and the relative reactivity of the ring cleavage are successfully explained. Further, their ionization potentials and electron affinities are discussed. In addition, the electronic distributions on the equatorial and axial forms of monosubstituted cyclobutane and cyclohexane are made explicit.

It is well known that aliphatic small-membered-ring compounds behave peculiarly in terms of their physico-chemical properties. Many experimental and theoretical studies of this subject have been carried out. It has been found, for example, that whenever cyclopropane derivatives are treated with iodine or bromine gas, 1, 3-dihalopropyl derivatives are separated readily.[1] Further, when hydrogen halides are added to cyclopropane, only propyl halogen compounds are obtained; these compounds are considered to be formed by the reaction following the Markownikoff rule.[2] Moreover, cyclopropane acts as a ligand with platinous salt complexes.[3]

These properties are characteristic of olefinic compounds, that is, of a double-bond nature. On the other hand, other cycloalkanes do not show the above chemical properties.

As to the physical properties, the absorption spectra of cyclopropane derivatives appear in rather a longer-wavelength region[4] than those of normal alkanes.

In the present paper, by applying the extended LCAO MO method proposed by Hoffmann[5] to three-, four-, five- and six-membered-ring compounds, the chemical and physical properties described above are studied on the basis of their calculated electronic structures.

Method of Calculation

A molecular orbital, φ, can be expressed as a linear combination of all the atomic orbitals, χ_r's, of the valence electrons of each constituting atom:[5]

$$\varphi = \sum_r C_r \chi_r \tag{1}$$

The simultaneous equations are written as follows:

$$\sum_{j=1}^{n} [H_{ij} - \varepsilon S_{ij}]C_j = 0 \quad (i = 1, 2, \cdots, n) \tag{2}$$

As to Coulomb integrals, H_{rr}'s, the values of the ionization potentials of the valence states of neutral atoms are used by reversing their signs,[6] as in Table 1. Resonance integrals, H_{rs}'s, are calculated by Eq. (3), with $K=1.75$:

$$H_{rs} = \frac{1}{2} K S_{rs}(H_{rr} + H_{ss}) \tag{3}$$

The overlap integrals, S_{rs}'s, in Eq. (3) are elucidated by the Slater-type atomic orbitals, the effective nuclear charges being taken as $Z_H = 1.0$, $Z_C = 3.25$ and $Z_{Cl} = 6.10$.

The values of the bond distances and bond angles for the individual compounds were taken from the literature[7] and are shown in Table 2. However, for compounds with a substituted group, the bond distances were taken, for the sake of simplicity, to be C–CH_3: 1.54 Å, and C–Cl: 1.76 Å.[*2]

[*1] Presented at the Meeting on the Electronic Structure of Molecules, October, 1965.

1) M. S. Kharasch, M. Z. Fineman and F. R. Mayo, *J. Am. Chem. Soc.*, **61**, 2139 (1939).

2) S. Nishida and T. Tsuji, *J. Soc. Org. Syn. Chem. Japan*, **22**, 272 (1964).

3) C. F. H. Tipper, *J. Chem. Soc.*, **1955**, 2045.

4) M. T. Rogers, *J. Am. Chem. Soc.*, **69**, 2544 (1947).

5) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

6) H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955).

7) "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 11, The Chemical Society, London (1958).

[*2] The structure shown in Fig. A, *i. e.*, the pseudo equatorial form, was adopted for monosubstituted cyclobutane. For monosubstituted cyclohexane, two kinds of structures, axial and equatorial, can be considered, but the equatorial configuration is slightly more stable, so it was adopted. Their calculated values will be given in the last part of this paper.

Fig. A

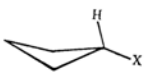


TABLE 1. VALUES OF COULOMB INTEGRALS OF ATOMIC ORBITALS[6)]

Unit: eV

	1s	2s	2p	3s	3p
H	−13.60	—	—	—	—
C	—	−21.43	−11.42	—	—
Cl	—	—	—	−25.26	−15.09

TABLE 2. INTERATOMIC DISTANCES (Å) AND BOND ANGLES[7)]

Cyclopropane	C-H	1.08
	C-C	1.54
	∠HCH	118.2°
Cyclobutane	C-H	1.098
	C-C	1.568
	∠HCH	114°
	The ring is nonplanar with dihedral angle 20°.	
Cyclopentane	C-H	1.09
	C-C	1.54
	The ring is planar.	
Cyclohexane	C-H	1.09
	C-C	1.53
	∠HCH=∠HCC=∠CCC=109.5°	
	The ring is in the chair form.	

Results and Discussion

Table 3 shows the energies of the highest occupied and the lowest vacant orbitals, and the energy gaps for cycloalkanes and their methyl derivatives, together with the observed ionization potentials.[8)]

The ionization potentials based upon the Koopman theorem are, in general, about 2 eV greater than the observed ones. In the extended Hückel calculations, however, the calculated ionization potentials are always larger. This discrepancy may be due to the parametrization of integrals and to the inexplicit consideration of the electron repulsion in the present approximation. Except for cyclopropane and its methyl derivative, a parallelism is observed between the calculated and experimental values. The calculated ionization potentials of cycloalkanes are a little larger than those of their methyl derivatives. These trends accord with the experimental results shown in Table 3.

The energy of the lowest vacant orbital becomes higher as the size of the ring increases: cyclohexane has approximately the same value as that of *n*-butane. This fact may be correlated with the fact that cyclohexane has the properties of normal saturated hydrocarbons (see Fig. 1). On the other hand, the energy of the lowest vacant orbital of cyclopropane becomes extraordinarily lower than those of the other cyclic compounds: cyclopropane can accept an electron much the most easily. This will be considered further later in this paper.

As is shown in Table 3, the energy gap is especially smaller in cyclopropane than in other cyclic compounds; there it is calculated to be 8.7 eV≈142 mμ. This value may be parallel with the maximum absorption wave length of cyclopropane, 6.4 eV≈195 mμ.[9,10)] We must refrain from entering into further discussion, since there exist, so far as we know, no experimental data for other cycloalkanes. It may, however, be noted that as the ring increases its members from three to six, the calculated energy gap becomes larger, indicating that the absorption spectra of the five- and six-membered rings become similar to that of *n*-butane.

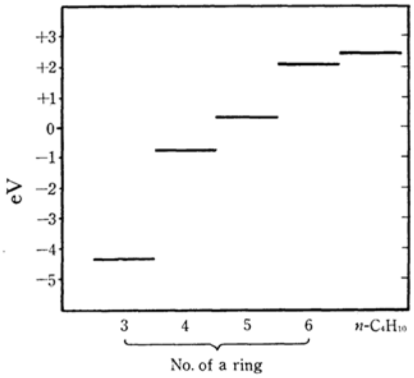


Fig. 1. Energy diagrams of the lowest vacant level of cycloalkanes.

Electronic Distribution. The partial atomic bond populations, n^{LV}_{AB}, of the lowest vacant orbitals are shown in Fig. 2. The n^i_{AB} value between A and B atoms in the *i*-th molecular orbital is a quantity shown by Eq. (4):

$$n^i_{AB} = 2\sum_{r}^{\text{on}A}\sum_{s}^{\text{on}B} \nu_i C_{ir} C_{is} S_{rs} \qquad (4)$$

where ν_i indicates the number of occupied electrons in the *i*-th molecular orbital,*3 where C_{ir} is the coefficient of the *r*-th atomic orbital belonging to the A atom in the *i*-th molecular orbital, and where S_{rs} is the overlap integral between the *r*-th and the *s*-th atomic orbitals.

As Fig. 2 shows, the partial atomic bond populations of the lowest vacant orbital*3 in cyclopropane are localized only in C–H bonds and are zero in C–H bonds.

[8)] a) J. L. Franklin, *J. Chem. Phys.*, **22**, 1304 (1954); b) R. F. Pottie, A. G. Harrison and F. P. Lossing, *J. Am. Chem. Soc.*, **83**, 3204 (1961).

[9)] A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

[10)] H. Weitkamp, U. Hasserodt and F. Korte, *Chem. Ber.*, **95**, 2280 (1962).

*3 In order to discuss the electronic structures of the anion radicals of cycloalkanes, the value of ν_{LV} in Eq. (4) is taken as 1.

TABLE 3. HIGHEST OCCUPIED, LOWEST VACANT ENERGY LEVELS, THEIR GAPS AND OBSERVED IONIZATION POTENTIALS OF CYCLOALKANES AND METHYL CYCLOALKANES

Compound	H. O. level eV	L. V. level eV	Gap eV	Ionization potential observed, eV
Cyclopropane	−13.052	−4.344	8.708	10.53,[a)] 10.23[b)]
Methyl cyclopropane	−12.612	−4.166	8.446	9.88[b)]
Cyclobutane	−12.658	−0.715	11.943	10.58[a)]
Methyl cyclobutane	−12.400	−0.659	11.741	—
Cyclopentane	−12.741	+0.338	13.079	10.92,[a)] 11.10[b)]
Methyl cyclopentane	−12.626	−0.101	12.525	10.45[a)]
Cyclohexane	−12.534	+2.085	14.619	10.50[a)]
Methyl cyclohexane	−12.493	+1.054	13.547	10.19,[a)] 10.40[b)]
n-Butane	−12.993	+2.492	15.485	10.90[c)]

a) R. F. Pottie, A. G. Harrison and F. P. Lossing, *J. Am. Chem. Soc.*, **83**, 3204 (1961).
b) J. L. Franklin, *J. Chem. Phys.*, **22**, 1304 (1954).
c) S. Oshima, *Bull. Japan Petrol. Inst.*, **3**, 56 (1961).

TABLE 4. BOND NATURES OF C–C AND C–H IN CYCLOALKANES

Compound	$Y_{CC'}$ %	Y_{CH} %	S-nature[13)] C–C, %	C–H, %	$J^{13}{}_{C-H}$[2)] cps	$P^2_{C(S)H(S)}$[14)]
Cyclopropane	9.08	35.82	19.53	30.49	161	0.0678
Cyclobutane	9.95	33.34	23.59	26.39	134	0.0601
Cyclopentane	11.99	31.14	25.00	25.00	128	0.0525
Cyclohexane	12.18	31.20	—	—	124	0.0519
n-Butane	12.86	30.19	25.00	25.00	—	—

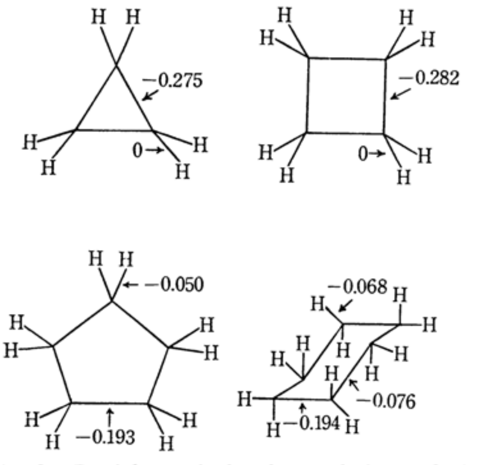


Fig. 2. Partial atomic bond populations of the lowest vacant orbital.

In fact, by ESR measurements, the anion radical of cyclopropane has been detected by Bowers and others.[11)] Their experimental results indicate that the odd electron of the cyclopropane anion radical is localized in the ring and does not exist in C–H bonds; this is in accordance with our theoretical result. On the other hand, the present calculations indicate that, in five- and six-membered rings, the lowest vacant orbital is localized in the C–H bond and that it is antibonding. Therefore, it may be concluded that it is difficult to form anion radicals of cycloalkanes the carbon numbers of which are more than four, while the fission of the C–H bond in these anion radicals will easily take place.

Nature of the Bond of Cycloalkanes. In order to examine further the properties of the bonds in the cyclic compounds, the $Y_{CC'}$ and Y_{CH} indices were defined as in Eqs. (5) and (6). They represent the contributions of the carbon 2s orbitals to the C–C and C–H bonds.

$$Y_{CC'} = \frac{N_{C(S)C'(S)}}{M_{CC'}} \times 100 \qquad (5)$$

$$Y_{CH} = \frac{N_{C(S)H(S)}}{M_{CH}} \times 100 \qquad (6)$$

M_{XY} is the atomic bond population[12)] of the bond between X and Y atoms, while $N_{C(S)C'(S)}$ and $N_{C(S)H(S)}$ are atomic orbital bond populations.[12)] The notations C(S) and C′(S) imply the 2s atomic orbitals of two different carbon atoms, and H(S)

[11)] K. W. Bowers and F. D. Greene, *J. Am. Chem. Soc.*, **85**, 2331 (1963).

[12)] K. Morokuma, H. Kato, T. Yonezawa and K. Fukui, This Bulletin, **38**, 1263 (1965).

indicates the 1s atomic orbital of the hydrogen atom.

Table 4 shows the values of $Y_{CC'}$ and Y_{CH}, the values of the s-nature*4 of carbon hybrids toward carbon and hydrogen atoms calculated by Coulson and Moffitt,13) the values of the ^{13}C–H coupling constant, and the squares of the bond order $P^2_{C(S)H(S)}$, where $P_{C(S)H(S)}$ indicates the bond order between the 2s orbital of a carbon atom and the ls orbital of a hydrogen atom:

$$P_{C(S)H(S)} = \sum_i^{occ} \nu_i C^i_{C(S)} C^i_{H(S)} \tag{7}$$

Table 4 indicates that the value of $Y_{CC'}$ increases as the size of the ring increases, in contrast to the case of Y_{CH}. Furthermore, in cyclopentane and cyclohexane, it has been found that these values are very close to those of *n*-butane. It may be noted that a satisfactory parallelism between $Y_{CC'}$ and Y_{CH} and the s-nature obtained by Coulson and Moffitt13) is also observed.

Besides, as to the nature of C–H bonds, there exists a linear relation between the s-nature of the hybridized orbital of a carbon and the ^{13}C–H coupling constants in the NMR spectrum. This fact is confirmed14) by the parallelism holding between the ^{13}C–H coupling constant and the $P^2_{C(S)H(S)}$ value obtained by the present approximation, which is an index representing the s-nature of a C–H bond in the molecular orbital theory.

Relative Reactivity of the Ring Cleavage. The atomic bond population, M_{XY}, of the C–C bonds of cycloalkanes and their methyl derivatives,*5 the dissociation energies of their C–C bonds as observed by Seubolt,15) and the free energy change, ΔG, in the C–C cleavage in the ring-opening polymerization obtained by Dainton and others16) are cited in Table 5.

The experimental results show that the C–C bond cleavage takes place more easily as the ring size decreases. As to relative difficulty of the ring cleavage, the larger the atomic bond population between the C–C bond in the ring, the larger becomes the overlap of the electronic cloud in that bond, thus making the bond firm.

It has been found that the values of M_{XY} increase as the size of a ring increases, causing the ring cleavage to become more difficult; these results agree completly with those of the experiments.*6

TABLE 5. RELATIVE REACTIVITY OF THE RING CLEAVAGE

Compound	$M_{CC'}$	Dissociation energy15) kcal/mol	ΔG16) kcal/mol
Cyclopropane	0.629	57	−22.1
CH_3-cyclopropane	0.652	—	−18.1
Cyclobutane	0.657	64	−21.5
CH_3-cyclobutane	0.681	—	−17.7
Cyclopentane	0.701	80	−2.2
CH_3-cyclopentane	0.733	—	+1.5
Cyclohexane	0.703	87	+1.4
CH_3-cyclohexane	0.754	—	+5.5

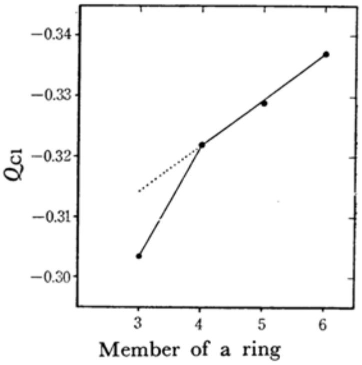


Fig. 3. Net charges on Cl atom of cycloalkyl chlorides.

Electronic Effect of Cycloalkane Rings. Figure 3 shows the relation between the net charges, Q_{Cl}'s, on the chlorine atom of chlorinated cycloalkanes and the number of the ring member. The net charge, Q_A, on the A atom is a quantity shown by Eq. (8):

$$Q_A = n_A - M_A \tag{8}$$

where n_A is the valence electron number of the

TABLE 6. DIPOLE MOMENTS OF CYCLOALKYL CHLORIDES

Compound	Observed18) Debye	Calcd Debye
Cl-cyclopropane	1.76	2.86
Cl-cyclobutane	—	3.42
Cl-cyclopentane	2.08	3.89
Cl-cyclohexane	2.10	4.18

[*4] The s-nature is represented by the quantity $(a^2/(a^2+b^2))\times 100$, where a and b are the coefficients in a hybridized orbital of the carbon atom $\varphi = a\chi_{2s} + b\chi_{2p\sigma}$.

13) C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949).

14) T. Yonezawa, I. Morishima, M. Fujii and K. Fukui, This Bulletin, **38**, 1224 (1965).

[*5] The M_{XY} of methyl cycloalkanes indicates the value of M_{XY} between the carbon atom attached to a methyl group and the adjacent carbon atom in the ring.

15) F. H. Seubolt, *J. Chem. Phys.*, **22**, 945 (1954).

16) F. S. Dainton, T. R. E. Devlin and P. A. Small, *Trans. Faraday Soc.*, **51**, 1710 (1955).

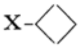
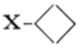
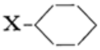
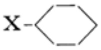
[*6] Here, we must remark on the so-called "strain energy" of cycloalkanes. From a consideration of the energy, cyclopropane seems to be the most stable. This fact is confirmed by the observed values of the heat of formation (F. S. Dainton, T. R. E. Devlin and P. A. Small, *Trans. Faraday Soc.*, **51**, 1710 (1955)). Therefore, the high reactivity of cyclopropane may be attributed to the nature of the C–C bond or C–H bond discussed in this section, but not to the "strain energy."

TABLE 7. ELECTRONIC STRUCTURES OF SUBSTITUTED CYCLOBUTANE AND CYCLOHEXANE

Total electronic energies

Compound	Equatorial, eV	Axial, eV	Compound	Equatorial, eV	Axial, eV
CH_3-cyclobutane	−522.06	−522.06	CH_3-cyclohexane	−730.41	−729.96
Cl-cyclobutane	−527.97	−527.90	Cl-cyclohexane	−736.18	−735.96

Electronic distribution

Compound	Dipole moment, D X=Cl	Q_X		M_{CX}	
		X=Cl	X=CH_3	X=Cl	X=CH_3
eq. 	3.419	−0.3224	−0.0014	0.6120	0.7311
ax. 	2.763	−0.3133	−0.0140	0.6249	0.7424
eq. 	4.188	−0.3370	−0.0269	0.6054	0.7103
ax. 	3.157	−0.3215	−0.0248	0.6105	0.7192

A atom and M_A is the atomic population[12] of the A atom.

$$M_A = 2\sum_{r}^{\text{on}A}\left[\sum_{i}^{\text{occ}} C_{ir}^2 + \sum_{i}^{\text{occ}}\sum_{s\neq r}^{\text{all}} C_{ir}C_{is}S_{rs}\right] \tag{9}$$

In Fig. 3, the net charge, Q_{Cl}, on the chlorine atom decreases as the size of a ring decreases; this tendency is even more remarkable in the cyclopropane ring. This seems to show that the smaller the size of a ring, the larger becomes the electron-attracting power*7 of the ring.

In fact, Roberts and Chambers[17] have concluded, by measuring the dissociation constants of cycloalkyl carboxylic acids or cycloalkyl amines and the dipole moments of cycloalkyl bromides, that the electron-accepting power of groups is in the order; cyclopropyl > cyclobutyl > cyclopentyl — cyclohexyl; the calculated results correspond fairly well with these experimental results.

The relations between the calculated and measured values of dipole moments of cycloalkyl chlorides are shown in Table 6. For the calculation of the dipole moment, $\boldsymbol{\mu}$, the following formula is used:

$$\boldsymbol{\mu} = e\sum_{A}^{\text{all}} Q_A\cdot\boldsymbol{r}_A \tag{10}$$

where $\boldsymbol{r}_A$ indicates the coordinate of the A atom.

Though an apparent parallelism between them is observed, the calculated values are larger by about 2 Debye (D) than the observed values.[18] This disagreement may be improved by adopting more suitable values for the Coulomb and resonance integrals or by using the ω-technique in the present approximations.

Electronic Structures of Monosubstituted Cycloalkanes. Hoffmann[5] has made calculations on the axial and equatorial configurations of methyl cyclohexane and has shown that the equatorial configuration is more stable by about 0.5 eV than the axial configuration; this is in conformity with the experimental results.

We have also calculated the total electronic energies, the net charges on substituted groups, X's, the atomic bond populations between carbon atoms and substituted groups, and the dipole moments for the two configurations.

As is shown in Table 7, for both compounds the equatorial configurations are more stable than the axial configurations. Actually, for example, methyl cyclohexane exists as a mixture of the equatorial and axial conformations in the ratio of 95 : 5.[19] For cyclohexyl chloride, the equatorial configuration is more stable than the axial one.[19] It must be stressed that the present approximation is successful to some extent in discussions on the difference in the electronic structures of the two configurations.

The calculations were carried out on the IBM 7090 at the Japan IBM Co., with the permission of the UNICON committee, whose kindness we hereby acknowledge.

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*7 For a detailed discussion of the electron-accepting power, the atomic orbital populations of the chlorine atom attached to the ring seem more suitable, since they represent the power resulting from the mesomeric effect and the inductive effect. This point will be further discussed in the future.

17) J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 5030 (1951).

18) a) M. T. Rogers and J. D. Roberts, *J. Am. Chem. Soc.*, **68**, 843 (1946).
b) "Constants of Organic Compounds," M. Kotake, The Asakura Publishing Co., Ltd., Tokyo (1963).

19) E. L. Eliel, N. L. Allinger, S. J. Angyal and G. A. Morrison, "Conformation Analysis," Interscience Publishers, John Wiley & Sons, New York (1965), pp. 436, 440.