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# Electronic Structures and Reactivities of Aliphatic Polycyclo Compounds. I. Fused Three-membered-ring Compounds*[1]

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The electronic structures of bicyclo(1.1.0)butane, tricyclo(3.1.0.0)hexane, tricyclo(2.1.0.0)-pentane, tricyclo(1.1.0.0)butane, prismane, and spiro(2.2)pentane are studied by the extended Hückel method. The calculated total energies of bicyclo(1.1.0)butanes with various dihedral angles, $\theta$, and bridgehead C–C–H angles, $\alpha$, show that the most stable configuration of bicyclobutane is at $\alpha=135°$ and $\theta=115$—$120°$. It is made clear that the s-nature of the carbon atoms of the C–H$_{\text{axial}}$ and C–H$_{\text{equatorial}}$ depends greatly on the dihedral angle of the two cyclopropane rings. The double-bond character between the bridgehead carbon atoms in the bicyclobutane and its homologues is pointed out. The stabilities of the C–C bonds of prismane are shown to be largely dependent on the angle between the C–H bond and the four-membered-ring plane. The electronic structures of some configurations of spiropentane with different dihedral angles are discussed. The physico-chemical properties of these compounds are briefly investigated.

It is well known that the cyclopropane ring has a small C–C–C bond angle of 60° and exhibits aromaticity and peculiar reactivities in most reactions.[1-3] Therefore, it is interesting to examine the physico-chemical properties of the following compounds: bicyclo(1.1.0)butane (I) in which two cyclopropane rings are fused with each other, with one C–C bond in common, and its homologues: tricyclo(3.1.0.0)-hexane (II), tricyclo(2.1.0.0)pentane (III) and tricylo(1.1.0.0)butane (IV), prismane (V), and spiro(2.2)pentane (VI), in which two cyclopropane rings hold a carbon atom in common.

Spiro(2.2)pentane (VI) was synthesized by Murray and Stevenson[4] about twenty years ago. The other compounds have, however, been prepared quite recently. The preparation of bicyclo(1.1.0)-butane (I) has been reported by Lemal *et al.*[5] and Srinivasan[6] independently. Tricyclo(3.1.0.0)-hexane and tricyclo(2.1.0.0)pentane derivatives were prepared by Meinwald[7] and by Masamune.[8] The preparation of tricyclo(1.1.0.0)butane, the structure of which seems to be tetrahedron, has not been reported as yet. Prismane derivatives have been synthesized by Viehe *et al.*,[9] and the properties of these small cage compounds have recently been reported on by Wiberg *et al.*[10]

As for theoretical investigations, Weltner[11] suggested that tricyclo(1.1.0.0)butane (IV) consists of "acetylenic" sp hybridized carbon atoms and

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*[1] Presented at the Meeting of Chemical Society of Japan (1966).

1) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

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

3) See for example, a) S. Nishida and T. Tsuji, *J. Soc. Org. Syn. Chem. Japan*, **22**, 272 (1964); b) M. T. Rogers, *J. Am. Chem. Soc.*, **69**, 2544 (1947); c) M. S. Kharasch, M. Z. Fineman and F. R. Mayo, *J. Am. Chem. Soc.*, **61**, 2139 (1939).

4) M. J. Murray and E. H. Stevenson, *J. Am. Chem. Soc.*, **66**, 812 (1944).

5) D. M. Lemal, F. Menger and G. W. Clark, *ibid.*, **85**, 2529 (1963).

6) R. Srinivasan, *ibid.*, **85**, 4045 (1963).

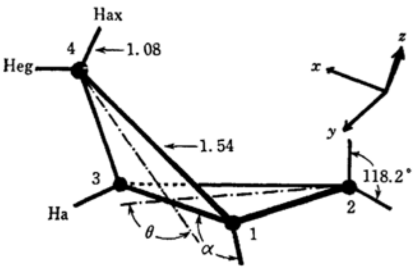
7) J. Meinwald, C. Swithenbank and A. Lewis, *ibid.*, **86**, 735 (1964).

8) S. Masamune, *ibid.*, **86**, 736 (1964).

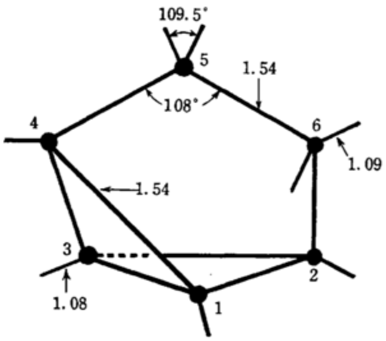
9) H. G. Viehe, R. Merényi, J. F. M. Oth, J. R. Senders and P. Valange, *Angew. Chem.*, **76**, 922 (1964).

10) K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965).

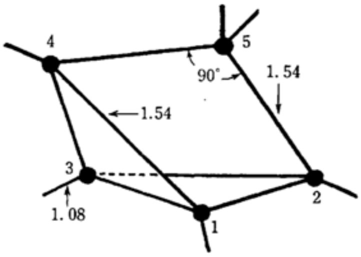
11) W. Weltner, Jr., *J. Am. Chem. Soc.*, **75**, 4224 (1953).



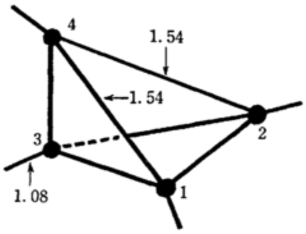
bicyclo[1.1.0]butane(I)



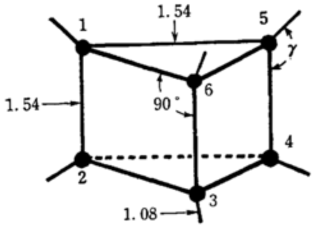
tricyclo[3.1.0.0.]hexane (II)



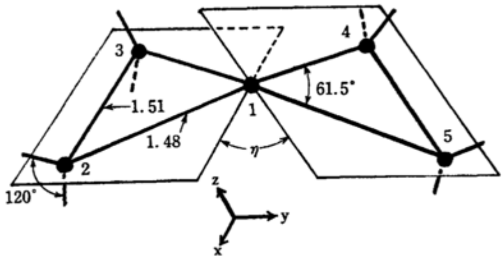
tricyclo[2.1.0.0.]pentane (III)



tricyclo[1.1.0.0.]butane (VI)



prismane (V)



Spiro[2.2] pentane (VI)

Fig. 1. Molecular structures of polycyclo compounds.

pointed out the large s-nature of the carbon atom in the C–H bond, basing his observations on the maximum overlap method.[12] Maksić *et al.*[13] calculated the electronic structure of bicyclobutane (I) by the same method and indicated the remarkable s-nature of bridgehead carbon atoms. Pomerantz *et al.*[14] suggested qualitatively that the central bond has an olefinic $\pi$-character.

Quite recently, Baird and Dewar[15] have calculated the strain energies of many cyclopropanes and cyclopropenes by means of the NDDO method[16] and be established that tricyclobutane (IV) would have very large strain energies (150.5 kcal/mol).

In the present paper, the correlation between the electronic structures and the dihedral angle of bicyclobutane will be studied first. Then, we will discuss how the electronic structures change for a series of bicyclobutane homologues: tricyclohexane (II), tricyclopentane (III), and tricyclobutane (IV). Secondly, the electronic structures of two possible configurations of prismane (V) will be investigated in relation to their stabilities. Finally, the stabilities of spiropentane (VI) with several dihedral angles will be discussed in comparison with that of 1,1-dimethylcyclopropane. The extended Hückel method[17] is used for the

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[12] For example, J. D. Dunitz and V. Schomaker, *J. Chem. Phys.*, **20**, 1703 (1952).

[13] Z. Maksić, L. Klasinc and M. Randić, *Theort. chim. Acta*, **4**, 273 (1966).

[14] M. Pomerantz and E. W. Abrahamson, *J. Am. Chem. Soc.*, **88**, 3970 (1966).

[15] a) M. J. S. Dewar and G. Klopman, *ibid.*, **89**, 3089 (1967); b) N. C. Baird and M. J. S. Dewar, *ibid.*, **89**, 3966 (1967).

[16] J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43**, S 136 (1965); **44**, 3289 (1966).

[17] R. Hoffmann, *ibid.*, **39**, 1397 (1958).

calculation. The parameters used in the present paper are identical with those previously reported.[17,18]

For all the compounds mentioned above except for spiro(2.2)pentane (VI)[19] the bond lengths and bond angles have never been reported. We assume them by referring to the observed values of cycloalkanes,[20] shown in Fig. 1.

**Electronic Structures of Various Configurations of Bicyclo(1.1.0)butane and Its Homologues.** *Stable Configuration of Bicyclo(1.1.0)-butane I.* The relation between the dihedral angle, $\theta$, and the total electronic energies of bicyclobutane with the constant value of $\alpha=180°$ is shown in Fig. 2. The calculated results indicate that the total electronic energy reaches a minimum at the dihedral angle, $\theta$, of 115—120°, while the bicyclobutane seems to be bent more than cyclobutane, which has the dihedral angle of 160°.

Next, the calculations were carried out, changing the value of the bridgehead C–C–H angle, $\alpha$, in the range of 90—180° but keeping the constant dihedral angle of 120°, which corresponds to a local minimum of total electronic energy. In Fig. 3 the total electronic energy of bicyclobutane is plotted against the value of $\alpha$. It is found that the total electronic energy has a minimum at an $\alpha$ value of about 135°.

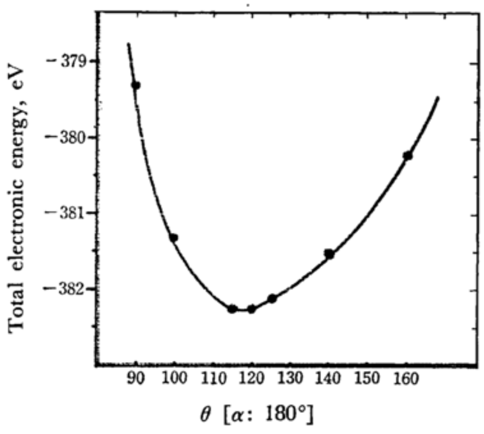

Fig. 2. Total electronic energies of various configurations of bicyclobutane.

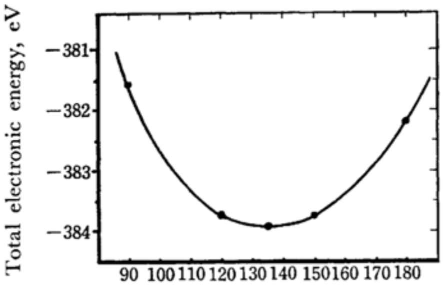

Fig. 3. Total electronic energies of various configurations of bicyclobutane.

As to the molecular structure of bicyclobutane, Haller and Srinivasan[21] suggested the following on the basis of their IR spectral data: $\theta=126°$, $\alpha=163°$, $\angle \mathrm{HCH}=118°$, $C_1$–$C_2$; 1.53 Å, $C_1$–$C_3$; 1.54 Å and C–H; 1.08 Å.

On the other hand, Harmony and Cox[22] have recently reported the following values, based on their microwave spectroscopic data: $\theta=121°$, $\alpha=130°$, $\angle \mathrm{HCH}=116°$, $C_1$–$C_2$; 1.51 Å, $C_1$–$C_3$; 1.49 Å and C–H; 1.08 Å. Our results seem to support the structure reported by Harmony and Cox.

*Stability of Bicyclo(1.1.0)butane and Its Homologues.* Tricyclo(3.1.0.0)hexane (II), tricyclo(2.1.0.0)-pentane (III), and tricyclo(1.1.0.0)butane (IV)*2 are considered to be cage molecules which are constructed by connecting perihedral secondary carbon atoms (*i. e.*, $C_2$ and $C_4$ in Fig. 1) with a ethylenic group, with a methylenic group, and directly.

Table 1 shows the dihedral angle, $\theta$; the bridgehead C–C–H angle, $\alpha$*3; the highest occupied HO orbital energy; the lowest vacant LV orbital energy, and the gap energy between these energies. The HO orbital energies of these compounds are about −11—−12 eV, as is shown in Table 1; they are higher by 1—2 eV than that of cyclopropane, whose HO orbital energy is −13.052 eV. The ionization potentials for these compounds seem to be smaller than that of cyclopropane. The LV orbital energies for these compounds are much lower than those for acyclic saturated hydrocarbons (*n*-butane, 2.492 eV; isobutane, 1.374 eV; neopentane, 0.837 eV); thus, the electron affinities of these compounds may be very large. These levels of bicyclobutane and its homologues, however, are higher than those of acyclic unsaturated hydrocarbons (*e. g.*, ethylene; −8.253 eV); therefore, the LV energy levels of these compounds are located midway between those for common saturated hydrocarbons and unsaturated hydrocarbons. The energy gaps between the HO and LV orbital energies for these compounds are 4—7 eV, much

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18) T. Yonezawa, K. Simizu and H. Kato, This Bulletin, **40**, 456 (1967).

19) J. Donohue, G. L. Humphrey and V. Schomaker, *J. Am. Chem. Soc.*, **67**, 332 (1945).

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

21) I. Haller and R. Srinivasan, *J. Chem. Phys.*, **41**, 2745 (1964).

22) M. D. Harmony and K. Cox, *J. Am. Chem. Soc.*, **88**, 5049 (1966).

*2 Tricyclo(1.1.0.0)butane (IV) has not as yet been synthesized.

*3 Since the configurations of bicyclobutane homologues have not yet been reported, as is mentioned above, the values of $\alpha$ are calculated from the configuration assumed in Fig. 1.

Table 1. Dihedral angles: $\theta$, $\alpha$, HO and LV energies and their gaps of bicyclobutane and its homologues

| Structural formula | Name | $\theta$ | $\alpha$ | HO energy eV | LV energy eV | Gap energy eV |
|---|---|---|---|---|---|---|
|  | Tricyclo(3.1.0.0)hexane (II) | 138°12′ | 121°43′ | −10.914 | −6.813 | 4.101 |
|  | Bicyclo(1.1.0)butane (I) | 120° | 135° | −11.950 | −5.904 | 6.046 |
|  | Tricyclo(2.1.0.0)pentane (III) | 109°28′ | 135° | −10.837 | −5.405 | 5.432 |
|  | Tricyclo(1.1.0.0)butane (IV) | 70°32′ | 144°14′ | −11.969 | −4.344 | 7.626 |

Table 2. HO and LV orbitals of bicyclobutane and its homologues

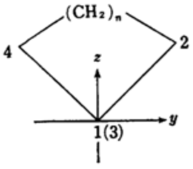
HO orbital

| Compound | $C_{1Z}+C_{3Z}$ | $C_{1X}-C_{3X}$[a] | $C_{2Z}-C_{4Z}$ |
|---|---|---|---|
| Tricyclo(3.1.0.0)hexane (II) | 0.4862 | 0.3474 | −0.2560 |
| Bicyclo(1.1.0)butane (I) | 0.4828 | 0.3843 | −0.2018 |
| Tricyclo(2.1.0.0)pentane (III) | 0.4537 | 0.2868 | −0.4225 |

LV orbital

| Compound | $C_{1Z}-C_{3Z}$ | $C_{1X}+C_{3X}$ | $C_{2X}+C_{4X}$ |
|---|---|---|---|
| Tricyclo(3.1.0.0)hexane (II) | 0.4851 | 0.4958 | −0.5275 |
| Bicyclo(1.1.0)butane (I) | 0.5785 | 0.4750 | −0.5089 |
| Tricyclo(2.1.0.0)pentane (III) | 0.5822 | 0.4957 | −0.5138 |

a) $C_1-C_3$ line denotes the $x$ axis. See Fig. 1.



$n=2,1,0$

less than that for cyclopropane (8.709 eV). It is well known that cyclopropane has its UV absorption spectra near the wavelength of 190 m$\mu$.[23] Therefore, the absorption spectra of present compounds exist in rather a longer wavelength region than those of cyclopropane, and their conjugative abilities may be large. The conjugative property will be discussed below.

*Nature of the Central Bond of Bicyclo(1.1.0)-butane and Its Homologues.* In this section the double-bond character of the central bonds ($C_1$–$C_3$ bonds in Fig. 1) of bicyclobutane and its homologues will be elucidated.

The AO coefficients of the HO and LV orbitals of the bicyclobutane with the most stable configuration and its homologues are cited in Table 2. They mainly consist of the $2p_Z$ and $2p_X$ of $C_1$, $C_2$, $C_3$ and $C_4$; other, very small AO coefficients are neglected.

These results indicated that a $\pi$-type interaction takes place between two $p_Z$ AO's of the carbon atoms in the central bonds of these compounds. Further, the HO and LV orbitals are respectively, the bonding and the antibonding orbital with respect to the $p_Z$–$p_Z$ bond. The natures of the two orbitals of these compounds resemble those of the $\pi$-orbitals of mono-olefins.

Wiberg *et al.*[10] have reported that the reaction of bicyclobutane-1-methanol with a dilute acid occurs almost instantaneously, accompanying the cleavage of the central bond, and that 1-hydroxycyclobutanemethanol is obtained. It is known that this addition reaction follows the Markownikoff rule.[10]

In addition, peculiar properties have been

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

observed in bicyclobutane, such as that the absorption spectra of methyl-3-methylbicyclobutane-1-carboxylate appears at 210 mμ (ε: 7000), just as in the corresponding α,β-unsaturated ester,10) and that the addition of iodine to bicyclobutane proceeds *via* an intermediate such as a benzene-iodine complex.10) Further, the derivatives of tricyclohexane (II) and tricyclopentane (III) with conjugative substituents on carbon atoms, $C_1$ and $C_3$, show their UV absorption spectra in rather a longer-wavelength region.8,24)

Our present conclusion, indicating the existence of the π-type conjugation in the central bond, is compatible with the suggestion of Pomerantz *et al.*,14) and it explains fairly well the above peculiar properties.

*s-Nature of the C-H Bonds of Bicyclo(1.1.0)butane and Its Homologues.* The s-nature of the bonds of bicyclobutane and its homologues has been studied in terms of $Y_{CH}$, which was difined in a previous paper18) as representing the contribution of the 2s AO of the carbon atom to the C-H bond:

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

where the notation C(S) implies the 2s AO of a carbon atom.

The relation between the values of $Y_{CH}$ and the dihedral angle, $\theta$, of bicyclobutane is shown in Fig. 4.

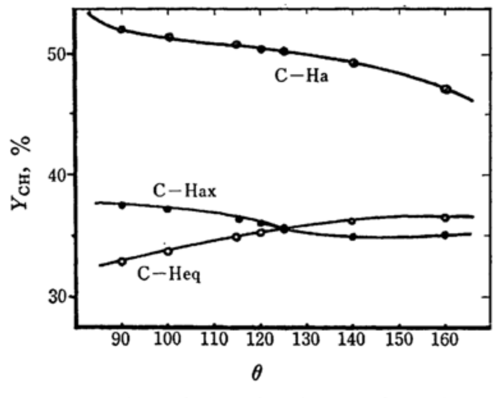


Fig. 4. Values of $Y_{CH}$ of various configurations of bicyclobutane.

The value of $Y_{CH_a}$ decreases with the increase in $\theta$. However, the value of $Y_{CH_a}$ is much larger than those of $Y_{CH_{axial}}$ and $Y_{CH_{equatorial}}$. Hence, the s-nature of the carbon-hybridized orbital of the C-$H_a$ bond may be expected to be large. The value of $Y_{CH_{axial}}$ decreases with the increase in $Y_{CH_{equatorial}}$ the two curves cross at the value of $\theta=125°$.

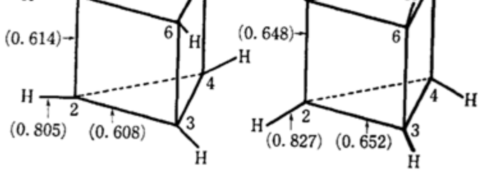
The observed $^{13}$C-H coupling constants,8,10,25,26) the fractional s-character of the carbon hybrid atomic orbital for the C-H bond estimated by experiments or from the values calculated by Weltner11) and Maksić *et al.*,13) the values of $Y_{CH}$, and the squares of the bond order, $(P_{CsHs})^2$, are given in Table 3, where $P_{CsHs}$ in dicates the bond order between the 2s orbital of the carbon atom and the ls orbital of the hydrogen atom in a C-H bond.

It may be seen in Table 3 that these theoretical indices run approximately parallel to the magnitude of the s-nature estimated and the $^{13}$C-H coupling constants. However, for C-H axial and C-H equatorial bonds in bicyclobutane, the calculated results contradict the $^{13}$C-H coupling constants.

However, it may be noted that, as has been stated above, the s-natures of these two C-H bonds very sensitively with the change in the dihedral angle and the two $Y_{CH}$ curves cross at 125°, which is very close to the dihedral angle, 120°, adopted in the present calculations. If, for the dihedral angle, the value of 126° reported by Haller and Srinivasan is adopted, our results agree with the experimental results. This point should be checked further both experimentally and theoretically with regard to the reliability of the extended Hückel approximation.

As to tricyclobutane (IV), the value of $Y_{CH}$ for its four equivalent C-H bonds amounts to 50%. This indicates the fractional s-character of the carbon hybrid AO in this compound is very large and that the C-H bond is markedly polar.

*Electronic Structures of Prismane (V).* Two structures of prismane were studied; one is a rather hypothetical configuration (V′), which consists of two interacting cyclopropenyl radicals, as is shown in Fig. 5. The other is a more real configuration



(V′) (V)

Fig. 5. Atomic populations and atomic bond populations of two configurations of prismane.
( ): atomic bond population

(V), where the C-H bonds of the cyclopropenyl radicals are bent to the outside. In Table 4 the total electronic energies and the energies of the highest occupied and lowest vacant orbitals of the two configurations of prismane ($C_6H_6$) are given,

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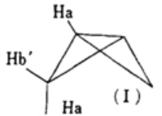
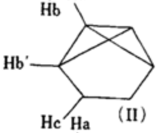
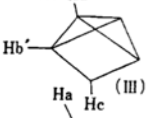
24) A. Small, *J. Am. Chem. Soc.*, **86**, 2091 (1964).

25) D. Seebach, *Angew. Chem.* **77**, 119 (1965); C. Juan and H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2198 (1962).

26) S. Masamune, *Tetrahedron Letters*, **1965**, 945.

TABLE 3. BOND NATURE OF C-H BONDS OF BICYCLOBUTANE AND ITS HOMOLOGUES

| Compnund | | $J^{13}{}_{\mathrm{C-H}}$ c/s | S-% estimated obs. | Present calcd. $Y_{\mathrm{CH}}$ % | Present calcd. $P^2$ |
|---|---|---|---|---|---|
|  (I) | Ha | 202[10] | 40.4<br>38.61[13] | 46.073 | 0.1104 |
| | Hb′ | 170[10] | 34 | 35.001 | 0.0637 |
| | Hb | 152[10] | 30.4 | 35.996 | 0.0685 |
|  (II) | Ha | — | — | 41.445 | 0.0907 |
| | Hb′ | 171[26]*a | 34.4 | 45.017 | 0.1059 |
| | Hc | — | — | 30.757 | 0.0504 |
|  (III) | Ha | — | — | 46.278 | 0.1096 |
| | Hb′ | 190[25]*a | 38 | 45.695 | 0.1074 |
| | Hc | — | — | 32.599 | 0.0566 |
|  (IV) | Ha | — | 32[11]<br>45.45[13] | 50.127 | 0.1263 |

*a Observed values of their derivatives are listed.

TABLE 4. TOTAL ELECTRONIC ENERGIES, HO AND LV ORBITAL ENERGIES OF TWO CONFIGURATIONS OF PRISMANE AND BENZENE

| | | Benzene | Prismane | |
|---|---|---|---|---|
| | | | V′ $\gamma$: 90° | V $\gamma$: 149° |
| Table electronic energy | eV | −527.825 | −513.977 | −521.209 |
| HO energy | eV | −12.820 | −11.514 | −11.368 |
| LV energy | eV | −8.361 | −6.167 | −1.167 |

TABLE 5. HO AND LV ORBITALS OF SOME CONFIGURATIONS OF SPIROPENTANE AND OF 1,1-DIMETHYL CYCLOPROPANE

HO orbitals

| | | |
|---|---|---|
| 1,1-Dimethylcyclopropane | | $0.5925C_{1\mathrm{X}} + 0.4210(C_{2\mathrm{Y}}-C_{3\mathrm{Y}}) - 0.2035(C_{5\mathrm{X}}+C_{4\mathrm{X}})$ |
| Spiropentane | $\eta=90°$ | $\left\{\begin{array}{l} 0.6058C_{1\mathrm{X}} + 0.4386(C_{2\mathrm{Y}}-C_{3\mathrm{Y}}) \\ 0.6058C_{1\mathrm{Z}} + 0.4386(C_{5\mathrm{Y}}-C_{4\mathrm{Y}}) \end{array}\right.$ |
| | $\eta=45°$ | $-\{0.2772C_{1\mathrm{X}}+0.3087(C_{2\mathrm{Y}}-C_{3\mathrm{Y}})\} + \{0.6691C_{1\mathrm{Z}}+0.3087(C_{5\mathrm{Y}}-C_{4\mathrm{Y}})\}$ |
| | $\eta=0°$ | $1.0118C_{1\mathrm{Z}}$ |

LV orbitals

| | | |
|---|---|---|
| 1,1-Dimethylcyclopropane | | $0.8101C_{1\mathrm{X}} - 0.6673(C_{2\mathrm{Y}}-C_{3\mathrm{Y}}) - 0.3928(C_{2\mathrm{X}}+C_{3\mathrm{X}})$ |
| Spiropentane | $\eta=90°$ | $\left\{\begin{array}{l} 0.8043C_{1\mathrm{X}} - 0.6550(C_{2\mathrm{Y}}-C_{3\mathrm{Y}}) - 0.4202(C_{2\mathrm{X}}+C_{2\mathrm{X}}) \\ 0.8043C_{1\mathrm{Z}} - 0.6550(C_{5\mathrm{Y}}-C_{4\mathrm{Y}}) - 0.4202(C_{5\mathrm{Z}}+C_{4\mathrm{Z}}) \end{array}\right.$ |
| | $\eta=45°$ | $-\{0.2723C_{1\mathrm{X}}-0.4800(C_{2}-C_{3\mathrm{Y}})\} + \{0.6574C_{1\mathrm{Z}}-0.4800(C_{5\mathrm{Y}}-C_{4\mathrm{Y}})\}$ |
| | $\eta=0°$ | $0.5761\{(C_{2\mathrm{Y}}-C_{3\mathrm{Y}})-(C_{5\mathrm{Y}}-C_{4\mathrm{Y}})\}$ |

together with those of benzene for comparison. The present calculations show that these two configurations of prismane are less stable than benzene and that the V configuration is more stable than the V′. Therefore, it may be concluded that the value of the C–C–H angle, $\gamma$, plays an important role in determining the stability of prismane. The highest occupied orbitals for both configurations are higher than that for benzene; the energy levels of the lowest vacant orbital for both configurations are higher by about 2 eV than that for benzene, but are markedly lower than those for ordinary saturated hydrocarbons (*e. g.*, *n*-butane, 2.492 eV) and for cyclopropane (−4.244 eV).

The atomic population and the atomic bond population of both configurations of prismane are given in Fig. 5.*4

*Photodecomposition of Prismane (V).* Breslow *et al.*27) proposed a reaction mechanism for the photodecomposition of prismane, where bicyclo(2.2.0)-hexa-1,5-diene is produced at first with cleavages of the $C_1$–$C_5$ and $C_2$–$C_4$ bonds, not of the $C_1$–$C_2$ bond, followed by isomerization to benzene. We assume this reaction in the following mechanism: the irradiation of light first causes the excitation of one electron from the HO orbital to the LV orbital, while in the next stage the cleavage of the weakest bond takes place. For this singlyexcited state, the values of $M_{C_1C_2}$ and $M_{C_1C_5}$ are obtained as 0.814 and 0.419 respectively. This implies that the cleavage of $C_1$–$C_5$ bond may occur more easily. These calculated results support the reaction mechanism proposed by Breslow *et al.*

**Electronic Structures of Spiro(2.2)pentane (VI).** As to spiro(2.2)pentane (VI), the dihedral angle, $\eta$, is experimentally known to be 90°. In the present treatment, the electronic structures for three configurations, with $\eta=90$, 45 and 0°, were investigated in order to reveal the correlation between the dihedral angle and the stability of spiro pentane. They were compared with the electronic structure of 1,1-dimethylcyclopropane, which is considered to be derived from spiropentane by opening one cyclopropane ring.

Spiropentane is the most stable at $\eta=90°$ ($-488.38$ eV) (this is in accordance with the experimental result) and gradually becomes more unstable as $\eta$ decreases from 90 ($-486.90$ eV) to 0° ($-484.09$ eV). The HO orbital energy for spiropentane with the configuration of $\eta=90°$ ($-12.551$ eV) is lower than that for 1,1-dimethylcyclopropane ($-12.325$ eV), but higher than those for methylcyclopropane ($-12.612$ eV) and for cyclopropane ($-13.052$ eV).

The AO coefficients of the HO and LV orbitals for spiropentane and dimethylcyclopropane are given in Table 5. In spiropentane with $\eta=90°$ both orbitals are doubly degenerated, and each orbital consists of the carbon 2p orbitals of a cyclopropane ring. The LV and HO orbitals at $\eta=45°$ are nearly equal to a linear combination of the corresponding doubly degenerated orbitals at $\eta=90°$. At the value of $\eta=0°$, the HO orbital is exclusively made of the $2p_Z$ AO of the carbon atom $C_1$, just as is a lone-pair orbital, further, the LV orbital is constructed only from the $2p_Y$AO's of the four carbon atoms, $C_4$, $C_5$, $C_2$ and $C_3$. Therefore, spiropentane of this configuration has extremely peculiar electron distribution.

An the basis of a comparison of the atomic bond populations, the $C_2$–$C_3$ bond for spiropentane ($M_{C_2C_3}=0.592$) may be expected to be weaker than those for 1,1-dimethylcyclopropane ($M_{C_2C_3}=0.611$) and cyclopropane ($M_{CC}=0.628$). In fact, in the hydrogenation which accompanies the ring-opening reaction, the heat of formation, $\Delta H$, for spiropentane is $-42.0$ kcal/mol, which seems to be required for the cleavage of the $C_2$–$C_3$ bond; on the other hand, the $\Delta H$ for cyclopropane is $-37.6$ kcal/mol.28)

These experimental results indicate that the cleavage of the $C_2$–$C_3$ bond occurs more easily in spiropentane than in cyclopropane; this is in accordance with our calculated results.

The calculations were carried out on the HITAC 5020 Computer at the University of Tokyo.

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*4 As prismane of the V′ configuration is transformed into the V configuration, all the atom bond populations increase and the value of $M_{cc}$ for a three-member ring becomes larger than that of cyclopropane, 0.629. This fact may also indicate that the bending of C-H bonds is closely correlated with the stabilization of prismane.

27) R. Breslow, P. Gal, H. W. Changand and L. J. Altman, *J. Am. Chem. Soc.*, **87**, 5139 (1965).

28) J. Newham, *Chem. Revs.*, **63**, 123 (1963).