An Ab Initio Molecular Orbital Study on the Conformations of Bicyclo[3.1.0]hexane Derivatives

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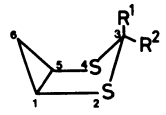
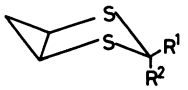
Ab initio calculations have been carried out for 2,4-dithia- (**5**), 2,4-dioxa- (**6**), 6-oxa- (**8**), 6-thiabicyclo[3.1.0]hexanes (**9**), bicyclo[3.1.0]hexane (**7**), and some of the corresponding cyclohexane derivatives **10—12** using 3-21G, 3-21G(*), and 6-13G* basis sets. Relative total energies and geometries have been obtained for both boat and chair forms of these compounds. The calculated geometries are in good agreement with observed ones for **7—9**. The boat form is more stable than the chair form in the bicyclic systems **7—9**, while both the forms have almost equal stability for **5** and the chair form of **6** is slightly more stable than the boat form. The relative stability of the boat form in the bicyclic systems compared with that in the monocyclic cyclohexane derivatives can be explained in terms of the stabilizing orbital interaction. Inversion barriers between the boat and chair forms for **5—7** have also been estimated and are briefly discussed. A similar calculation for bicyclo[3.2.0]hept-6-ene also shows that the boat form is much more stable than the chair form contrary to the conclusion derived from the analysis of experimental results.

In our previous study on stereoselective reactions of carbanions of dithiabicyclo[3.1.0]hexanes, we performed ab initio calculations of the dithiabicyclohexanes and the corresponding dithianes and revealed that the carbanion **1** of boat form is most stable among isomeric carbanions **1—4** and that the boat and chair forms of the corresponding neutral molecules **5B** and **5C** have almost equal stability.[1] The structures of similar bicyclic systems, such as bicyclo[3.1.0]hexane (**7**),[2] 6-oxabicyclo[3.1.0]hexane (**8**),[3] and 6-thiabicyclo[3.1.0]hexane (**9**),[4] have been determined spectroscopically to be a boat form. These computational and experimental results suggest that the high stability of the boat form is a general trend in bicyclo[3.1.0]hexane systems, which stands in a sharp contrast to the well-established fact that the chair form is much more stable in the case of the corresponding monocyclic six-membered systems.[5]





1	R^1=H, R^2=—	**3**	R^1=H, R^2=—
2	R^1=—, R^2=H	**4**	R^1=—, R^2=H
5B	R^1=R^2=H	**5C**	R^1=R^2=H

We have become interested in why the boat form in the bicyclic systems has relatively high stability in spite of the unfavorable steric interaction between inward hydrogens on C_3 and C_6, and have carried out accurate ab initio geometry optimizations on these bicyclohexane derivatives and some related compounds. The main purpose of this account is to elucidate the factors determining the stability of the boat form from the standpoint of orbital interaction. We also report on inversion barriers between boat and chair forms in some representative bicyclohexane systems.[6]

Computational Details. The geometries for all the structures considered were completely optimized by energy gradient method at the Hartree-Fock level of theory. The standard split-valence 3-21G and 3-21G(*) basis sets (including a set of d-type polarization functions for sulfur atoms) were used in these optimizations. This level of theory has been demonstrated

Table 1. Relative Energies (kcal mol^{-1}) of Compounds **5—13**

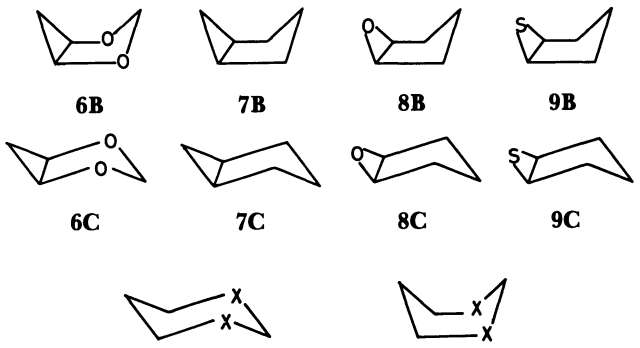
Compound	3-21G	3-21G(*)	6-31G*	Compound	3-21G	3-21G(*)	6-31G*
5B	0.1	0.0[b]	0.0[c]	**9C**	4.1	4.3	4.5
5C	0.0[a]	0.5	0.0	**10B**	7.6		7.9
6B	0.4		0.9	**10C**	0.0[m]		0.0[n]
6C	0.0[d]		0.0[e]	**11B**	5.3		6.6
7B	0.0[f]		0.0[g]	**11C**	0.0[o]		0.0[p]
7C	3.1		3.3	**12B**	4.4	5.5	5.5
8B	0.0[h]		0.0[i]	**12C**	0.0[q]	0.0[r]	0.0[s]
8C	3.9		3.8	**13B**	0.0[t]		0.0[u]
9B	0.0[j]	0.0[k]	0.0[l]	**13C**	5.8		5.4

a) −945.1732 hartree. b) −945.3897 hartree. c) −949.9442 hartree. d) −302.9175 hartree. e) −304.6136 hartree. f) −231.7045 hartree. g) −233.0001 hartree. h) −267.3151 hartree. i) −268.8144 hartree. j) −588.4676 hartree. k) −588.5693 hartree. l) −591.4921 hartree. m) −232.9169 hartree. n) −234.2076 hartree. o) −304.1405 hartree. p) −305.8302 hartree. q) −946.3860 hartree. r) −946.6008 hartree. s) −951.1499 hartree. t) −269.3375 hartree. u) −270.8410 hartree.

to be reliable in the calculation of molecular geometries for a wide variety of systems.[7] In order to obtain more reliable energy estimates we have repeated the calculations with 6-31G* basis at the 3-21G or 3-21G(*) optimized geometries.

Calculated Relative Energies and Geometries. Relative energies obtained for **5**—**12** are listed in Table 1. The pertinent points in Table 1 are as follows: (1) For monocyclic systems **10**—**12**, the chair form is much more stable than the boat form, as is well known experimentally.[5] (2) In contrast to the monocyclic systems, the boat form is definitely more stable than the chair form in the bicyclic systems **7**—**9** where the five-membered ring consists of only carbon atoms. This also agrees with the experimental results that each of them exists only as a boat-form conformation.[2-4] (3) For bicyclic compounds having heteroatoms at 2- and 4-positions, **5** and **6**, although the stability of a boat form becomes less pronounced than in the case of **7**—**9**, the boat form has the stability almost equal to the chair form in the sulfur heterocycle **5**, and the boat form of the oxygen heterocycle **6** is very slightly less stable than its chair form.

Comparison of Calculated and Observed Geometries. Calculated geometries obtained for **5**—**9** are listed in Table 2[8] along with the observed geometries for **7**—**9**. As mentioned previously each of **7**—**9** has been reported to exist as the boat conformer in keeping with the present calculations. The calculated geometries are in good agreement with the experimental ones with the only exception of C_1—C_5 bond length of **7B** where the calculated value is longer than the observed one by 0.06 Å. The reason for this discrepancy has not been clear up to the present. There are some interesting features in the geometries of these compounds. (1) The angles between the planes $C_1C_5X_6$ and $C_1X_2X_4C_5$ (X=C, O, or S) in **5**, **6**, **7**, and **9** (denoted as α hereafter) are almost constant, ca. 110°, while those for **8B** and **8C** are 103—105°. (2) The angle between the planes $C_1X_2X_4C_5$ and $X_2C_3X_4$ (X=C, O, or S) (denoted as β hereafter) is constant, 150—152°, in the boat form except for 161° in **6B**. In the chair form, however, those having carbon atoms at 2- and 4-positions have β of 161° while those having heteroatoms at these positions have a smaller β (151—154°). (3) When the boat form is more stable than the chair form, β in the boat form is always smaller than β in the chair form. Conversely, when the chair form is more stable than the boat form, β in the chair form is smaller than that in the boat form. In an intermediate case where both the boat and chair forms have a



10 X=CH_2
11 X=O
12 X=S

Table 2. Bond Lengths (Å) and Bond Angles (deg) in **5**—**9** and **13** as Determined by Calculations (3-21G or 3-21G(*))[a,b]

Compd	X_2–C_1 (X_4–C_5)	X_2–C_3 (X_4–C_3)	C_1–C_6[c] (C_5–C_6)	C_1–C_5	X_6–H_3[d]	$\angle C_1X_2C_3$ ($\angle C_5X_4C_3$)	$\angle\alpha$[e]	$\angle\beta$[e]
5B	1.784	1.824	1.513	1.511	2.663	96.0	113.1	149.8
5C	1.790	1.824	1.511	1.511		96.8	110.8	149.8
6B	1.427	1.440	1.516	1.490	2.470	107.9	111.6	161.4
6C	1.432	1.438	1.510	1.499		107.1	109.3	153.6
7B	1.524	1.554	1.514	1.515	2.231	104.7	110.3	149.7
	(1.543)	(1.543)	(1.515)	(1.454)			(109.4)	(154.8)
7C	1.527	1.559	1.512	1.515		105.7	109.8	160.9
8B	1.512	1.557	1.477	1.472	2.683	103.9	104.3	151.8
	(1.513)	(1.53)	(1.443)	(1.482)		(104.0)	(104.7)	(152.3)
8C	1.516	1.561	1.477	1.475		105.0	103.4	160.6
9B	1.526	1.554	1.828	1.493	2.937	104.5	110.7	150.3
	(1.513)	(1.530)	(1.819)	(1.471)			(110—120)	(150)
9C	1.532	1.561	1.826	1.493		105.2	110.3	160.9
13B[f]	1.537	1.550	1.537	1.599		105.1	114.2	145.0
13C[f]	1.542	1.559	1.540	1.593		106.8	114.6	160.9

a) Calculations were carried out for **5** and **9** with 3-21G(*) and for **6**—**8** and **13** with 3-21G basis. b) Values in parentheses for **7B**, **8B**, and **9B** are observed values. c) C_1–C_7 for **13**. d) This represents the distance between the two inward hydrogens on C_3 and C_6 for **5B**, **6B**, and **7B**, and that between the inward hydrogen on C_3 and the heteroatom at 6-position for **8B** and **9B**. e) α and β are dihedral angles between two planes $C_1C_6C_5$ and $C_1X_2X_4C_5$ and between two planes $X_2C_3X_4$ and $C_1X_2X_4C_5$, respectively. f) C_6–C_7 is 1.326 and 1.325 Å for **13B** and **13C** respectively.

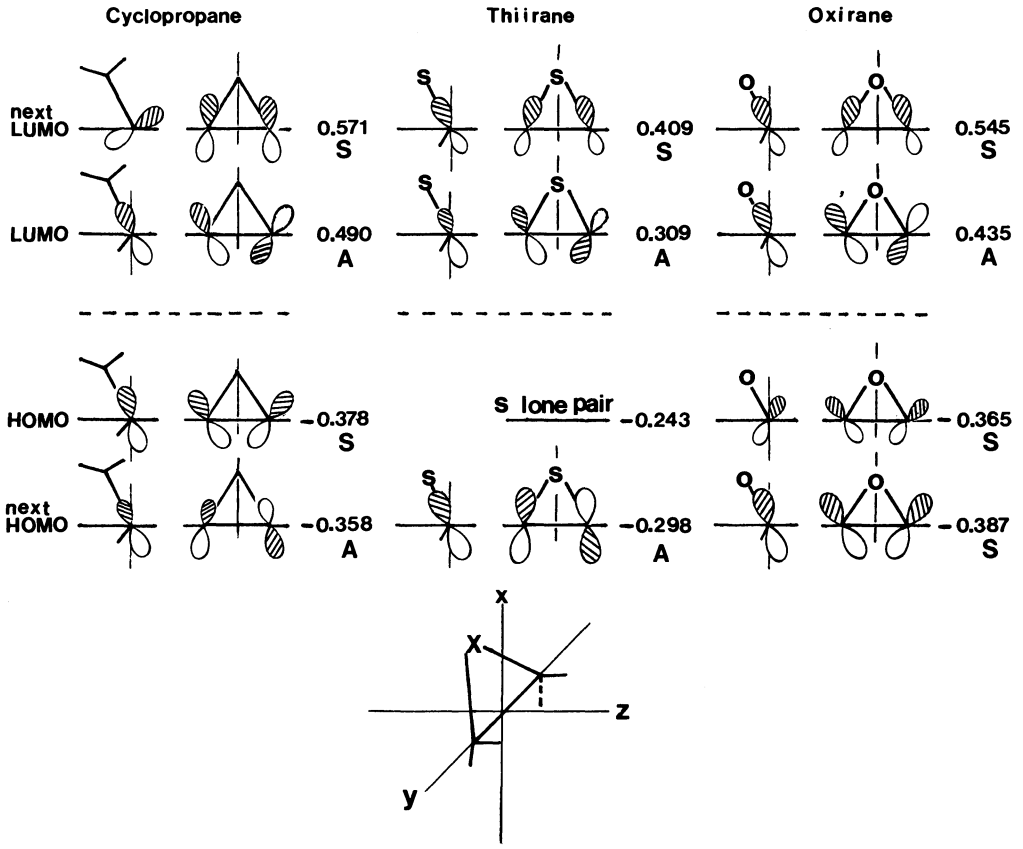


Fig. 1. Some important molecular orbitals in cyclopropane, thiirane, and oxirane.

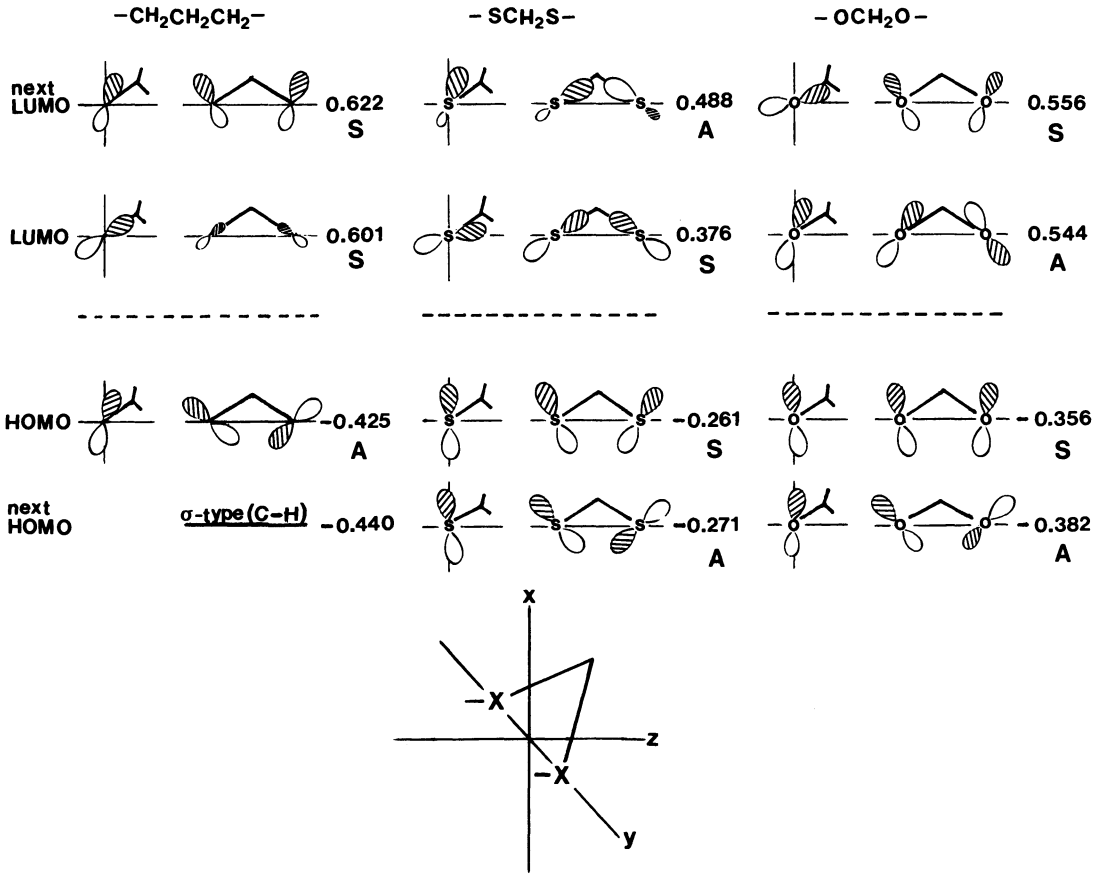


Fig. 2. Some important molecular orbitals in $HXCH_2XH$ moiety (X=CH_2, S, O).

similar stability, β's in the both forms are similar. (4) As for bond lengths, there is no essential difference between those for the boat and the chair conformers.

Rationale for the High Stability of Boat Forms. In view of the high stability of a chair form of monocyclic six-membered systems, it is remarkable that the boat form is highly stabilized in bicyclohexane systems. Although the chair form is more stable than the boat form in the case of **6**, the difference in energy between the two conformers is only 0.9 kcal mol^{-1}, which is much smaller than the corresponding difference for **11**, i.e., 6.6 kcal mol^{-1}.

In order to explain this high stabilization of the boat form, we have considered the orbital interactions between the three membered ring and the XCH_2X parts (X=CH_2, O, S). In Figs. 1 and 2 are shown some occupied and unoccupied orbitals of these parts pertinent to the following discussion.

The figures indicate that there exists an in-phase orbital interaction between LUMO of the three-membered ring and HOMO or next HOMO of the XCH_2X group. This orbital interaction mainly contributes to the relative stabilization of the boat form. On the other hand, in the chair forms such an efficient orbital interaction cannot exist, because the downside lobe of HOMO (or next HOMO) on the XCH_2X group is tilted outward in contrast with the case of the boat form as illustrated in Fig. 3 with **5** as an example.

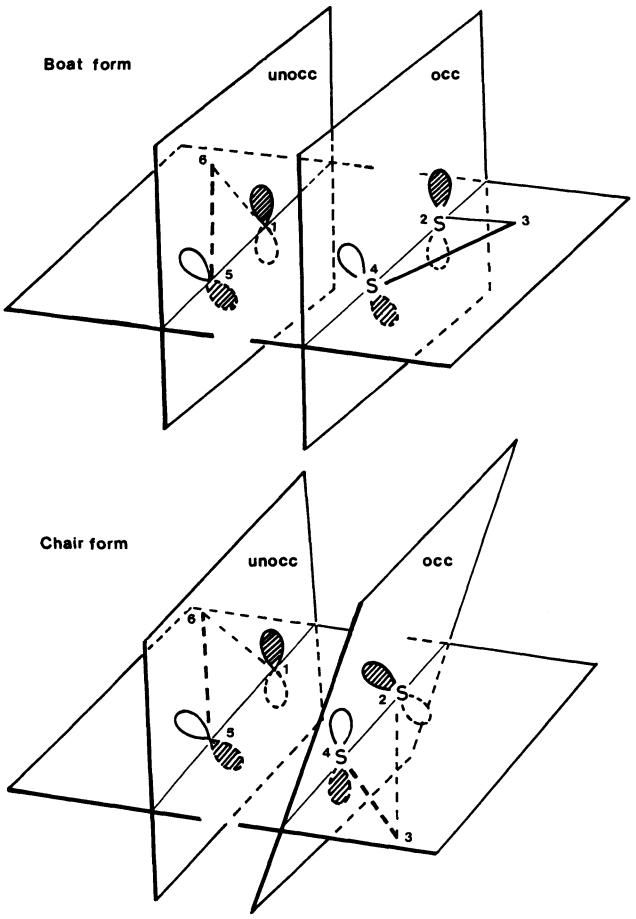


Fig. 3. Molecular orbital interaction between cyclopropane and SCH_2S moieties in **5B** and **5C**.

Dithiabicyclohexane 5B and Dioxabicyclohexane 6B: In **5B**, the most favorable interaction is that between LUMO on C_1—C_5 (antisymmetric, denoted as (A) hereafter) of the cyclopropane and the next HOMO of the lone pair on sulfur atoms, (A), of SCH_2S moiety the orbital energy of which is very close to that of HOMO (Fig. 2). The cyclopropane HOMO (S)-SCH_2S LUMO(S) interaction is also conceivable but it is not efficient because the lobe of LUMO on sulfur atoms is pointed to the direction almost perpendicular to the cyclopropane orbital.

The stabilizing interaction in **6B** is similar to that of **5B** except that the HOMO–LUMO energy difference is larger because of the higher electronegativity of oxygen. This larger difference is probably responsible for the less stability of the boat form **6B** than **5B**.

6-X-Bicyclohexanes (X=CH_2, O, S), 7B, 8B, and 9B: In **7B**, there exists an in-phase interaction between cyclopropane LUMO (A) and large back lobes (HOMO(A)) of pseudo-equatorial C-H bonds at 2- and 4-positions. The stabilization of the boat form is mainly attributed to this type of interaction. The cyclopropane HOMO(S)-$CH_2CH_2CH_2$ LUMO(S) cannot cause the stabilization, because LUMO of $CH_2CH_2CH_2$ moiety is directed toward C_1-C_2 (or C_4-C_5) bond axis(i.e., z-axis). As can be seen from HOMO and LUMO of ethylene oxide and ethylene sulfide shown in Fig. 1, the stabilizing interaction in **8B** and **9B** can be explained in a manner similar to **7B**, namely, the interaction between cyclopropane-like Walsh-type orbital and the back lobes of C-H bonds at 2- and 4-positions.

The higher stability of cyclohexane **10C** vs. **10B** has traditionally been explained in terms of the two pairs of unfavorable eclipsed interaction in the CH_2CH_2 bond and the steric repulsion between inward hydrogens of the bow and stern carbons in the boat form.[9] Inspection of the molecular model of bicyclo[3.1.0]-hexane suggests that the former type of eclipsed interaction exists between C_1H and quasi-equatorial C_2H in the chair form, **7C**, while the relationship between those hydrogens becomes gauche in the boat form, **7B**. The relative stability of **7B** vs. **7C** has exclusively been attributed to this type of unfavorable interaction in **7C**.[10] However, the latter type of steric interaction between inward hydrogens on C_1 and C_4 in **10B** should be more conspicuous in **7B** because the presence of the cyclopropane ring makes the distance between inward hydrogens on C_3 and C_6 shorter as judged by the molecular model. The calculated geometries of **10B** and **7B** also support the above argument since the distance in question is 2.355 Å in

10B and 2.231 Å in **7B** which is rather close to the sum of the van der Waals radii of two hydrogen atoms. This implies that the boat forms in **7—9** must be stabilized by some other factors in spite of this severe repulsive interaction. It is strongly suggested, therefore, that the above-mentioned stabilization due to stereoelectronic effect plays an important role in these compounds. In this connection, it is interesting that β in the boat form is always smaller than β in the chair form when the boat form is more stable than the chair form (see point (3) in the previous section). Since the HOMO–LUMO interaction becomes more effective in parallel with decrease of β in **7B**, **8B**, and **9B**, the values of β are considered to become small in spite of the repulsive interaction between C_3H–C_6H (or C_3H–X_6 lone pair). The reason for the large β value in **6B** is not very clear at present, but it is most likely that the large β is a consequence of a compromise between the HOMO–LUMO interaction and C_3H–C_6H repulsion which becomes relatively serious in this case because of shorter C–O (1.427 and 1.440 Å) than C–C bond distances (1.524 and 1.554 Å).

Conformation of Bicyclo[3.2.0]hept-6-ene. Chiang and Bauer studied the structure of bicyclo[3.2.0]hept-6-ene (**13**) by microwave spectroscopy and reported that it has a chair form.[11] In view of the above-mentioned general trend that bicyclo[3.1.0]hexane

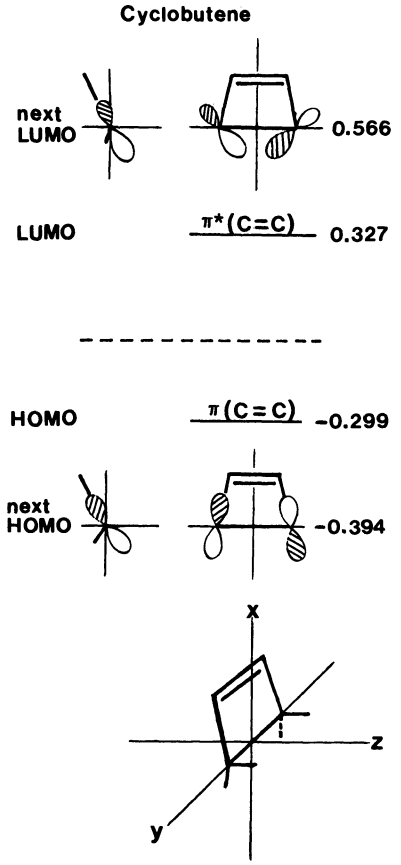
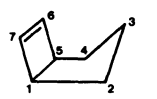
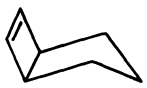


Fig. 4. Some important molecular orbitals in cyclobutene.



13B



13C

derivatives have a boat form, we have become interested in why the bicycloheptene **13** prefers the chair form to the boat form and have carried out ab initio calculations for this compound. The results are shown in Tables 1 and 2. The calculation indicates that the boat form is obviously more stable than the chair form, and indeed here again exists the stabilizing interaction between the cyclobutene ring and the $(CH_2)_3$ moiety similar to that for **7B** discussed above (Figs. 2 and 4). In view of the fact that the present calculations correctly reproduce experimental results both in the relative energies and geometries of **7—9**, we think that there is some room for doubt in the structual analysis of Chiang and Bauer and reexamination of the structure of **13** is highly desirable.

Energy Barrier of Boat-Chair Interconversion. In order to obtain information on the barrier of boat-chair interconversion, we have carried out ab initio calculations for the representative bicyclic systems, **5**, **6**, and **7**. In the calculations, atoms 1, 2, 4, and 5 are fixed on the same plane and atom 3 is fixed so as to be x Å apart from the plane. Under this constraint geometry optimizations have been performed at several x values. As can be seen from Fig. 5, the barrier height for the boat–chair conversion of **6** and **7** are almost zero in each case and hence it is suggested that the boat form of **6** and the chair form of **7** actually cannot exist as a stable conformer. In the case of **5** there is a definite barrier for interconversion between the boat and chair forms. However, it is so small that each conformer is considered to be able to undergo

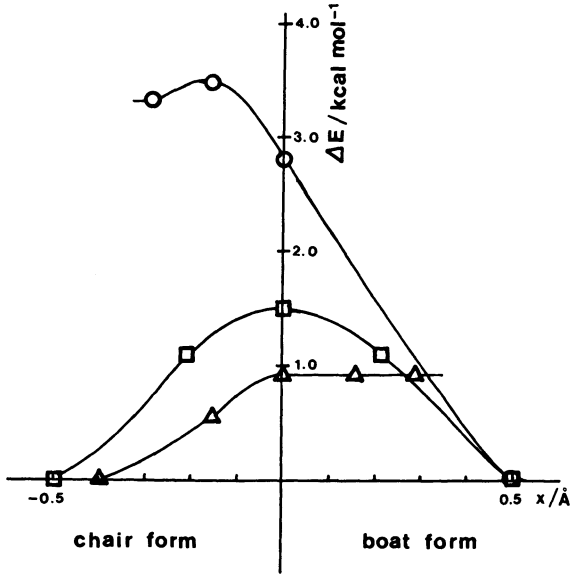


Fig. 5. Energy barrier of boat-chair interconversion in **5**, **6**, and **7**. □: **5**, △: **6**, ○: **7**.

almost free interconversion at least at ambient temperature.[12]

Conclusion

Relative energies and geometries have been calculated by ab initio method for boat and chair forms of bicyclohexane derivertives **5**—**9**. Contrary to monocyclic cyclohexane derivatives **10**—**12** which exist as a chair conformer, the stability of a boat form is much increased in the bicyclic compounds and in the case of **7**—**9** the boat conformer becomes a more stable one. The stability of the boat conformer has been found to result from the stabilizing orbital interaction between HOMO of the three-membered ring and LUMO of the $Y_3CH_2Y_4$(Y=CH_2, O, or S) group. Calculation on bicyclo[3.2.0]-hept-6-ene has revealed that the boat conformer is preferred again in this case contrary to the conclusion derived from the experimental result, thus necessitating reexamination of the structural analysis of this compound. Calculated energy barriers for **5**—**7** have indicated that **6** and **7** exist only as the chair and boat forms, respectively, while **5** undergoes free interconversion between the boat and chair conformers.

The numerical calculations were carried out with the IMSPACK program at the Nagoya University Computation Center.

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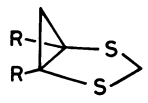
12) The NMR spectra of dithiabicyclohexanes I and II[1] have indicated that there is no essential change between 20 °C and −70 °C. It suggests that freezing of the flipping of the five membered ring does not occur at least at −70 °C, consistent with the present calculations.



I: R = CH_3
II: RR = $(CH{=}CH)_2$