

NMR and Theoretical Study on Conformation of Methacrolein Dimer, 2,5-Dimethyl-3,4-dihydro-2H-pyran-2-carboxyaldehyde

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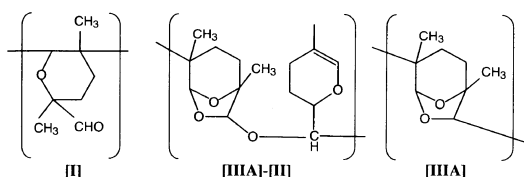
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ABSTRACT: Detailed structures of methacrolein dimer (MAD) were analyzed by nuclear magnetic resonance (NMR) and theoretical calculations. Two dimensional ¹H and ¹³C NMR peaks were assigned. Relative stability of conformations and interconversion barrier height were studied by semi-empirical MNDO and *ab initio* DFT calculations. Barrier height between pseudoaxial and pseudoequatorial half-chair conformers was 5.8 kcal mol⁻¹. Separations of chemical shifts of two protons bonded to the same methylene carbons became larger as measurement temperature decreased, due to reduced mobility of the ring framework.

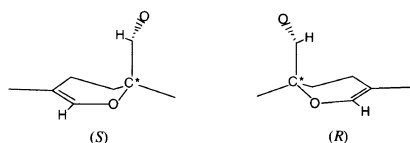
KEY WORDS ¹³C Nuclear Magnetic Resonance / ¹H Nuclear Magnetic Resonance / Methacrolein Dimer / Conformational Analysis / Theoretical Calculations /

Cationic polymerizations of alkenes are important for preparation of commercial polymers. While many polymers of simple α -olefins are obtained by these processes, polymers with cyclic structures in the backbone are limited. Cationic polymerization of methacrolein dimer (MAD) (2,5-dimethyl-3,4-dihydro-2H-pyran-2-carboxyaldehyde) gives bicyclic polymer [III A] in good yield at ambient temperature among other possible polymer structures shown below.^{1,2} (For notations of polymer structures, see these references.)



As MAD became available from several sources at present, polymerization mechanism and conditions of such a unique polymer were studied again in this paper.

MAD has an asymmetric carbon in the ring to which the aldehyde group is bonded. Therefore, MAD has two stereo isomers (enantiomers *S* and *R*) and each isomer takes several conformations arising from ring puckering deformation and rotation of the aldehyde group around the C*–CHO axis.



As a result of torsional constraint imposed by the double bond in the ring framework, conformational variation in the 3,4-dihydropyran ring is rather limited compared to the oxycyclohexane ring such as pyranose. MAD is also important in oligosaccharides synthesis,^{3,4} but information about the structures and reactivities is surprisingly scarce. In early works, Bushweller and O'Neil assumed the predominant existence of a half-chair conformer for 3,4-dihydropyran based on nuclear magnetic resonance (NMR) spectra⁵ in another NMR measurement, Eliel *et al.*^{6,7} reported analysis of MAD structures by use of ¹³C and ¹H NMR, but did not give detailed assignments of CH₂ and CH₃.

3,4-Dihydropyran has been analyzed theoretically only by the force field approach but there is no study on MAD. Force field studies are appropriate for hydrocarbons such as cyclohexane and cyclohexene, but simple force field potential does not well account for oxygen lone pair and double bond π -electron effects. Highly accurate *ab initio* calculation is indispensable for determination of the conformer geometries and precise prediction of the barrier height.

This paper focuses on conformational preference and interconversion of MAD molecule after successful assignment of ¹H and ¹³C NMR peaks of MAD. Various conformers of MAD and the interconversion barrier height were determined by electronic structure calculations. NMR and computational results herein set foundations for the reactivity of MAD in cationic polymerization and are discussed in our sequel papers.

EXPERIMENTAL

Preparation of Methacrolein Dimer

MAD was prepared by thermal dimerization of dry methacrolein in the presence of hydroquinone (1% by weight in methacrolein) at 160°C for 3 h under nitrogen

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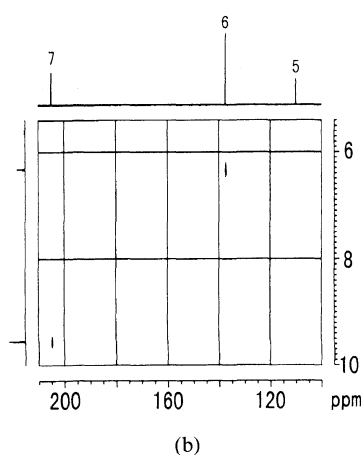
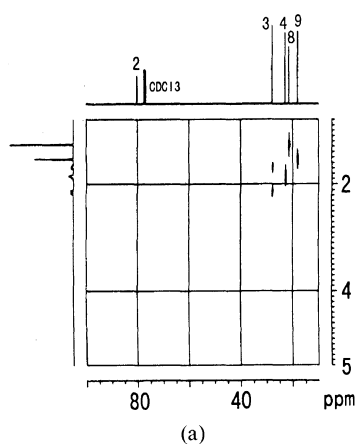


Figure 1. CH correlation spectrum of MAD. Numbers on the one dimensional ^{13}C spectrum are based on the structure of MAD appeared in a text. (a) methyl, methylene region; (b) methine region.

pressure and fractionated at 68.1°C under 24 mm Hg.

Method for NMR Measurements

10–100 mg MAD were dissolved in 0.7 ml chloroform- d_1 , and ^1H and ^{13}C NMR spectra were recorded with a BRUKER DPX400 spectrometer operated at ^1H frequency of 400 MHz at room temperature, except for INADEQUATE and variable temperature experiments. INADEQUATE was performed by dissolving 300 mg samples in 0.5 ml chloroform- d_1 with a JEOL JNM-EX270 spectrometer operating at 270 MHz at 30°C . Tetramethylsilane (TMS) peak at 0 ppm was used as reference for the spectra. This paper analyzes variable temperature ^1H NMR spectra at 30, 0, -55 , and -80°C by dissolving 10 mg samples in toluene- d_8 , with the JEOL spectrometer equipped with a temperature controller. The samples were stabilized at the measurement temperature at least 15 min before measurement. Methyl peak of toluene at 2.3 ppm was used as reference for the spectra.

Details of Electronic Structure Calculations

Electronic structures were calculated at semi-empirical MNDO/AM1 and *ab initio* Density Functional Theory (DFT) levels. Total energy for a molecule is calculated with these methodologies in UniChem/MNDO94 and UniChem/Dgauss programs, running on SGI/Cray J90 and T90 systems⁸. DFT calculations were based on the

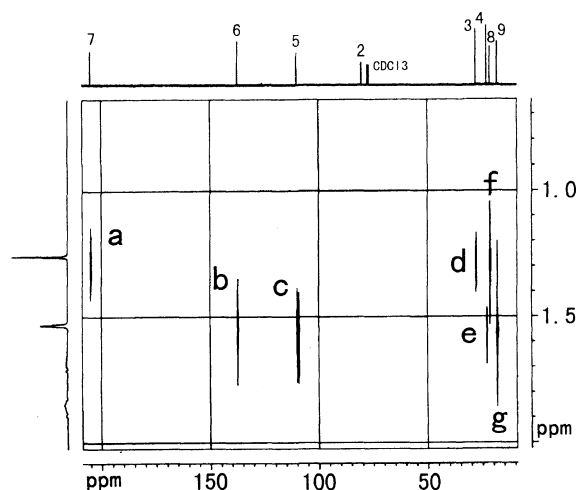


Figure 2. COLOC spectrum of MAD.

self-consistent, non-local DFT formalism of Becke–Perdew⁹ with valence double zeta plus polarization basis functions (DZVP/A1).⁸ Molecular geometries are optimized by the same method.

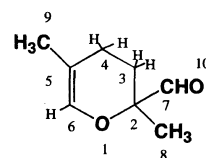
RESULTS AND DISCUSSION

Assignments of ^{13}C and ^1H NMR Spectra of MAD

To fully understand conformational change of the MAD molecule, complete assignment must be made at first. MAD has two methylene carbons and two methyl carbons in almost the same magnetic environment, and thus 2D NMR spectroscopy was necessary.

Figure 1 shows two dimensional ^1H – ^{13}C correlation spectra with the corresponding ^1H and ^{13}C one dimensional spectra. Protons and carbons of the unsaturated methine (6.33, 137.4 ppm) and aldehyde group (9.55, 205.0 ppm), as well as unsaturated (110.0 ppm) and saturated (80.2 ppm) quaternary carbons are readily assigned. Two protons connected to the methylene carbon at 28.0 ppm appear separately at 1.7 and 2.1 ppm while those connected to the other methylene carbon have almost the same frequency.

To make clear the assignments of proton peaks of methyl and especially methylene groups, ^1H – ^{13}C correlation *via* long-range (COLOC) spectrum of MAD was measured. Figure 2 shows five long-range correlation peaks in addition to direct coupling peaks *f* and *g*. Peak *a* shows long-range coupling of C8 methyl protons with the aldehyde carbon, while peak *b* that of C9 methyl protons with C6 methine carbon as shown below.



Resonance at 1.26 ppm in ^1H spectrum was thus assigned to C8 methyl protons, and resonance at 1.53 ppm C9 methyl protons. Peak *c* shows correlation between C9 methyl protons and C5 quaternary carbon.

Peaks *d* and *e* show long-range couplings of the methylene carbon at 28.0 ppm to C9 methyl protons and

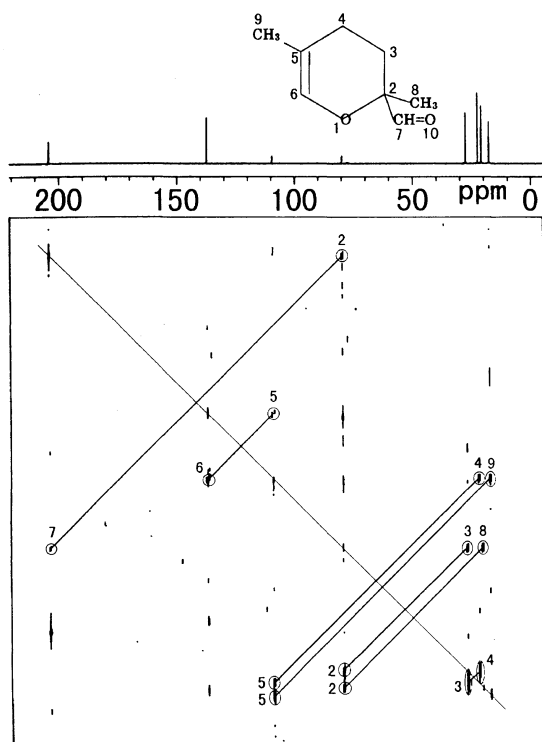


Figure 3. INADEQUATE spectrum of MAD with its structure. Connectivity of carbon atoms is represented by 7 bold lines.

Table I. Data for assignments of NMR spectra of MAD (in chloroform- d_1 , 30°C)

Position ^a	¹³ C NMR		¹ H NMR ^d	
	Chemical shift/ppm ^b	Atomic group ^c	Chemical shift/ppm	Intensity
2	80.2	C	—	0
3	28.0	CH ₂	1.7 2.1	1 1
4	23.0	CH ₂	1.85	2
5	110.0	C	—	0
6	137.4	CH	6.33	1
7	205.0	CH	9.55	1
8	21.5	CH ₃	1.26	3
9	18.2	CH ₃	1.53	3

^a Based on the structure of MAD in the text. ^b Complete decoupled ¹³C NMR. ^c Results of DEPT experiments. ^d ¹H NMR, CH correlation.

the other methylene carbon at 23.0 ppm to C8 methyl protons. Thus the former carbon is assigned to C4 methylene carbon, while the latter to C3 methylene carbon.

Assignments of carbon resonances were clarified by 2D-INADEQUATE spectrum as shown in Figure 3. The observed connectivities in the INADEQUATE spectrum are depicted in the figure. The results are consistent with those obtained by COLOC method. ¹H and ¹³C chemical shifts are summarized in Table I.

Low Temperature NMR Measurement and Interconversion of Two Conformers

Although basic assignments of NMR spectra were made in chloroform for comparison with the spectrum of polymer recorded in the past, variable temperature

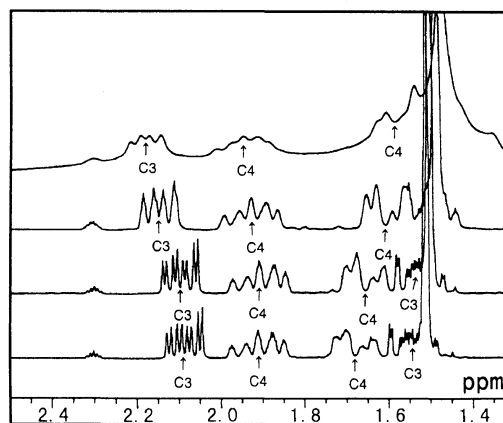
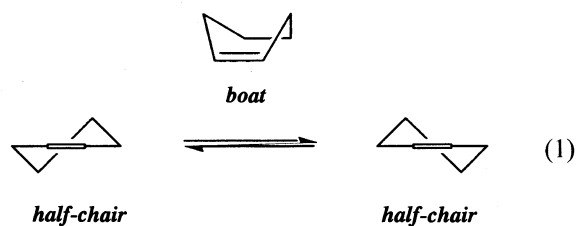


Figure 4. ¹H NMR spectra of MAD in toluene- d_8 at +30, 0, -55, and -80°C (from bottom to top).

measurement demanded measurement in another solvent with lower freezing point than that of chloroform. ¹H spectra in toluene- d_8 at low temperature down to -80°C are shown in Figure 4. Spectrum pattern of methylene region in toluene was different from that in chloroform. ¹H resonances of C3 methylene were found at 1.5 and 2.1 ppm, while those of C4 methylene at 1.7 and 1.9 ppm at 30°C. This assignment was confirmed by the CH correlation spectrum and ¹³C NMR spectrum, which showed almost the same pattern despite differences in solvents. These shifts come from differences in two protons bonded to methylene carbons. C3 methylene protons closer to the aldehyde group give larger differences of chemical shifts than that of C4 ones at each temperature. When interconversion occurs between pseudoaxial and pseudoequatorial conformers, the differences become smaller as a result of averaged magnetic environment of the two protons. The differences were larger with decreasing temperature down to -80°C, suggesting more frozen interconversion with temperature decrease. Activation energy of this interconversion was estimated by *ab initio* calculations (*vide infra*).

Calibration of Theoretical Calculation with Cyclohexene

In unsaturated six-membered ring molecules, structures of cyclohexene have been extensively studied by spectroscopy (IR, NMR) and theoretical computations (force field, electronic structure calculations). It is generally accepted that cyclohexene exists in half-chair conformers (C₂ point group symmetry) and these conformers interchange *via* the boat structure¹⁰ (eq 1).



These half-chairs and boat conformers are sometimes called twist and bent structures, respectively.¹¹ Anet *et al.* estimated the energy barrier for interconversion to be 5.3–5.6 kcal mol⁻¹ by dynamic NMR measurement and 5.4–5.7 kcal mol⁻¹ by theoretical calculations.¹² It is

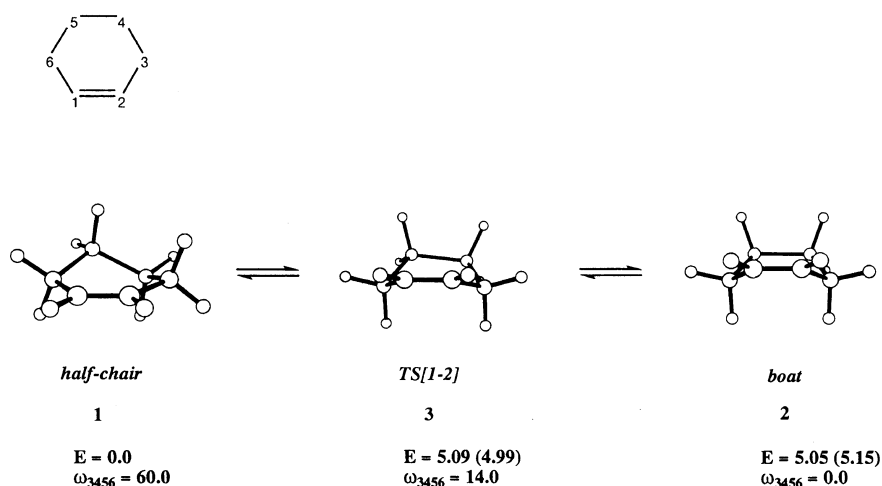


Figure 5. Relative stability of conformers in cyclohexene ring inversion process. Molecular structures are optimized by non-local DFT calculations. Energy values are total energy in DFT calculation and total energy plus ZPE correction (in parenthesis). Unit in kcal mol⁻¹ and °C.

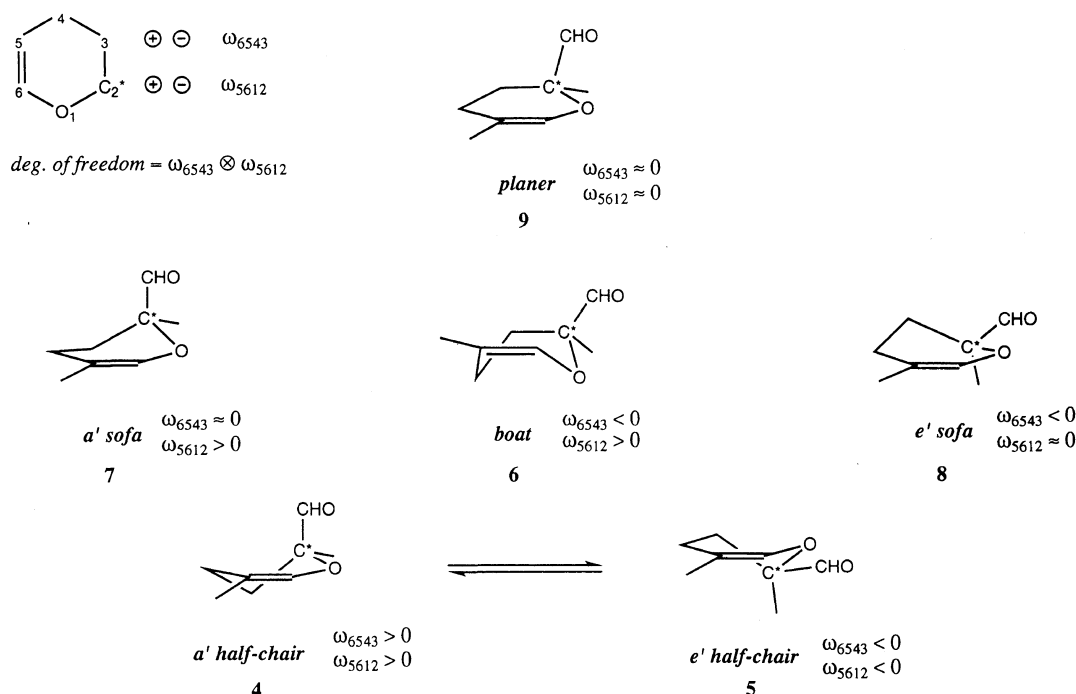


Figure 6. Two-dimensional potential energy surface (PES) scan scheme for 3,4-dihydropyran ring framework. Possible conformers of MAD are designated by two dihedral angles, ω_{6543} and ω_{5612} , on the PES.

also argued by several authors that the symmetric boat form (C_s point group symmetry) is either a transition state between the two half-chair conformers or an intermediate state and real transition states exist in-between the half-chair and boat forms. This point is not clear, but information up to now suggests instability of the boat form. This study calculated interconversion barrier height of cyclohexene for comparison with those in other works. We carried out potential energy surface (PES) scans with selected degrees of freedom and MNDO/AM1 calculations. Obtained critical points at the MNDO/AM1 PES are re-optimized with non-local DFT calculations. Final conformer geometries and energies for cyclohexene are given in Figure 5.

The results in Figure 5 are somewhat confusing. DFT energy suggests that the boat form is a shallow minimum, *i.e.*, intermediate with very small differences in energy

($\Delta E = 0.04$ kcal mol⁻¹), along the interconversion pathway to vicinal real transition state. However, if zero point energy (ZPE) correction is added to pure DFT energy, the transition state is slightly more stable than the intermediate state.

In summary, our results show a very flat topped energy profile in agreement with the previous work by Anet *et al.* The barrier height was 5.2 kcal mol⁻¹ based on ZPE corrected value. The same method was used in the following theoretical calculation of MAD.

Conformational Analysis of MAD

Due to the asymmetric carbon in the ring, MAD exists in two isomer forms, enantiomers of each other. This study dealt with only the *S* form.

The geometry and energetics of MAD ring framework are studied analogously to the conformational analysis

of cyclohexene. Half-chair, boat, sofa, and planer forms are possible as local minima or transition states.¹⁰ The sofa and planer forms are not likely critical point geometries for the 3,4-dihydropyran ring, but several local minima of the sofa were reported for pyran derivatives.¹³

To cover all candidate conformers, this paper set up two-dimensional PES scans as shown in Figure 6 and calculated at MNDO/AM1. In this scheme, two dihedral

angles, ω_{6543} and ω_{5612} , were varied by 5 deg at each step. Rotation of the aldehyde group was treated separately. Figure 7 shows the obtained energy profile for ring deformation. PES clearly designates two minima, corresponding to the half-chair conformers. The transition state occurs around $\omega_{5612} \sim 0$ and $\omega_{6543} < 0$. The lowest energy path seems to connect the half-chair minima *via* the boat/sofa transition state. The planer form is neither a stable nor transitional state (TS). It is

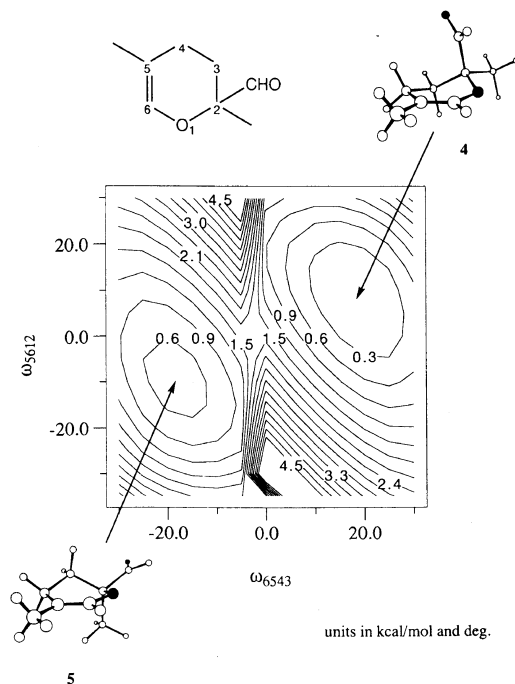
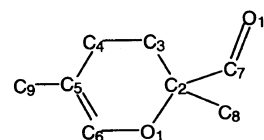


Figure 7. Two-dimensional potential energy surface (PES) of MAD calculated with MNDO/AM1 method.

Table II. Selected dihedral angles of MAD conformers (degree)



<i>trans</i> a' half-chair (4A)		<i>trans</i> e' half-chair (5A)	
C5-C6-O1-C2	13.6	C5-C6-O1-C2	-11.8
C6-C5-C4-C3	12.5	C6-C5-C4-C3	-14.9
O1-C2-C7-O10	-175.6	O1-C2-C7-O10	171.0
O1-C2-C3-C4	58.3	O1-C2-C3-C4	-57.8
Boat (6A)		Boat (6B)	
C5-C6-O1-C2	40.4	C5-C6-O1-C2	40.4
C6-C5-C4-C3	-37.1	C6-C5-C4-C3	-37.1
O1-C2-C7-O10	-170.9	O1-C2-C7-O10	-2.3
O1-C2-C3-C4	8.3	O1-C2-C3-C4	8.3
<i>cis</i> a' half-chair (4B)		<i>cis</i> e' half-chair (5B)	
C5-C6-O1-C2	15.5	C5-C6-O1-C2	-12.3
C6-C5-C4-C3	13.6	C6-C5-C4-C3	-13.7
O1-C2-C7-O10	5.4	O1-C2-C7-O10	0.0
O1-C2-C3-C4	58.1	O1-C2-C3-C4	-58.2
TS [4A-4B]a		TS [5A-5B]a	
O1-C2-C7-O10	-57.6	O1-C2-C7-O10	-41.0
TS [4A-4B]b		TS [5A-5B]b	
O1-C2-C7-O10	67.0	O1-C2-C7-O10	58.0

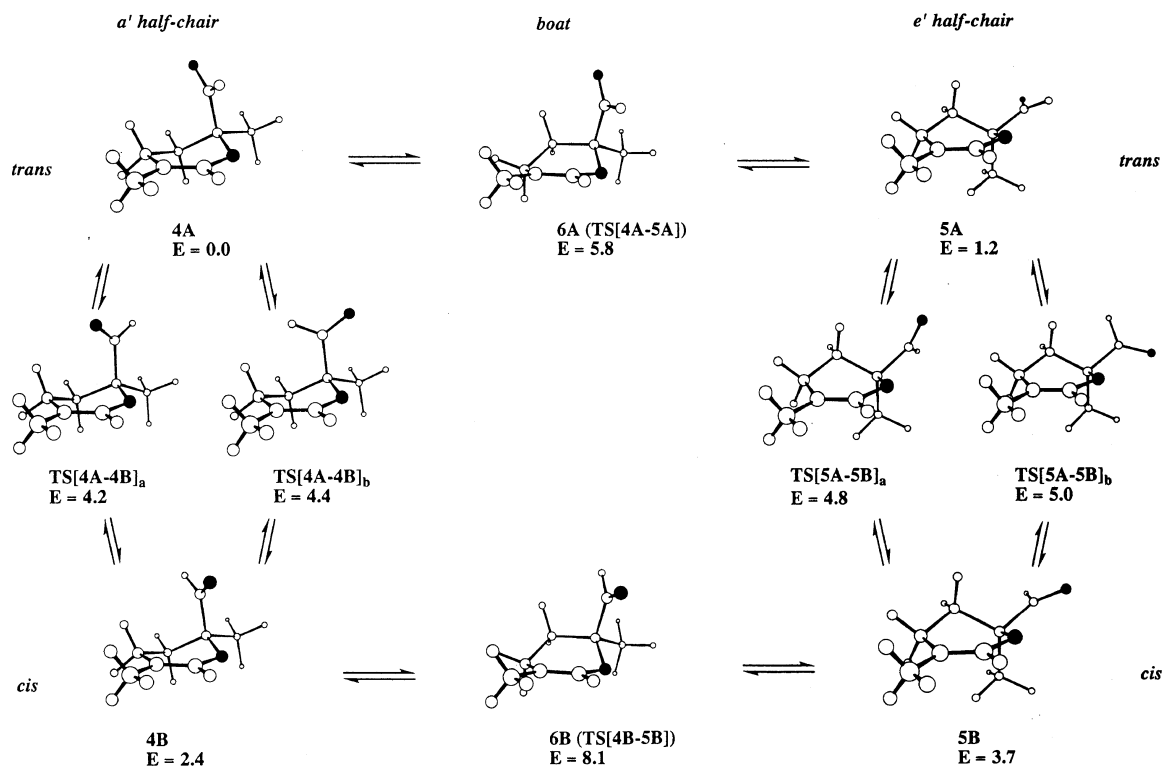


Figure 8. Relative stability of MAD conformers located by non-local DFT calculations. Energy values are corrected for ZPE. a' and e' denote pseudoaxial and pseudoequatorial position of the aldehyde group, respectively, and are used to designate half-chair conformers. *trans* and *cis* denote relative positions of the aldehyde to the ring oxygen.

not clear from these PES with which the TS geometry is similar, *i.e.*, boat or sofa, and whether boat/sofa like local minimum exists as an intermediate. Thus two half-chair geometries and boat/sofa forms were optimized by *ab initio* DFT calculations, giving only two half-chair local minima and the boat transition state. For each geometry thus obtained, transition states for the aldehyde group rotation were located. The final results are shown in Figure 8. Selected geometric parameters for these geometries are given in Table II. In Figure 8 and Table II, abbreviations *a'* (pseudoaxial) and *e'* (pseudoequatorial) are used to discriminate the two half-chair conformers. Also *cis* and *trans* positions of the aldehyde oxygen to the ring oxygen are denoted by A and B, respectively, to designate these conformers.

The interconversion scheme in Figure 8 comprises 4 local minima, 4A, 4B, 5A, and 5B, and transition states connecting these structures. In *a'* and *e'* transformation, the boat structure is located as the transition state. In rotational transformations (4A to 4B and 5A to 5B), we located two transition states for each.

trans a' half-chair (4A) is more stable than *e'*-form (5A) and *cis a'* half-chair (4B) by 1.2 kcal mol⁻¹ and 2.4 kcal mol⁻¹, respectively. *cis e'* half-chair form (5B) is rather unstable. Assuming Boltzman distribution, the ratios of these conformers are 4A/5A/4B = 1/0.14/0.019 (30°C) and 1/0.044/0.0021 (-80°C).

Barrier height for the ring inversion from the most stable 4A to 5A and that for the aldehyde group rotation from 4A to 4B were calculated to be 5.8 kcal mol⁻¹ and 4.2 kcal mol⁻¹, respectively. Thus calculated ring inversion barrier height of MAD is comparable with or slightly higher than that of cyclohexene (5.2 kcal mol⁻¹, section 3). Bushweller and O'Neil reported the interconversion free energy barrier for cyclohexene and 3,4-dihydropyran to be 5.2 kcal mol⁻¹ (-165°C) and 6.6 ± 0.3 kcal mol⁻¹ (-140°C), respectively.⁵

MAD in this paper is in good agreement with or slightly lower (0.8 kcal mol⁻¹) than the barrier height for 3,4-dihydropyran. Both works agree that 3,4-dihydro-

pyran ring has higher interconversion barrier than cyclohexene.

NMR measurement suggests that these conformers interchange rather freely at 30°C. Although calculated PES shows that both ring puckering and aldehyde group rotation have interconversion barrier, NMR suggests that the ring motion becomes freezed by lowering the temperature. Above results show that at -80°C the *trans a'* half-chair form (4A) exists predominantly.

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