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The Conformations of (Z)-2,3,4,7,8,9-Hexahydrooxonin and (Z)-Cyclononene. X-Ray Structure Determinations of Isolaurallene and Neolaurallene, and Force-Field Calculations

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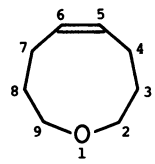
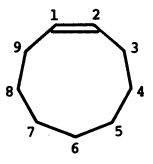
The molecular structures of isolaurallene and neolaurallene, diastereomeric nonterpenoids ($C_{15}H_{20}O_2Br_2$) from the red algae *Laurencia*, have been determined by X-ray crystallographic analysis. The crystal data are as follows: isolaurallene, orthorhombic, space group $P2_12_12_1$, a=10.393(2), b=27.824(4), c=5.397(1) Å, Z=4, D_c=1.669 g cm^{-3}; neolaurallene, monoclinic, space group $P2_1$, a=13.338(7), b=4.929(1), c=12.435(5) Å, β=98.22(4)°, Z=2, D_c=1.609 g cm^{-3}. The structures were solved by the heavy-atom method, and refined by the block-diagonal least-squares method; the final R-values were 0.076 and 0.069 respectively. The (*Z*)-2,3,4,7,8,9-hexahydrooxonin rings in the two substances possess essentially the same conformation. The MM2 force-field calculations have shown that this conformation is almost identical to the most stable one of the 11 minimum-energy conformations found for (*Z*)-2,3,4,7,8,9-hexahydrooxonin. For comparison, the conformations of (*Z*)-cyclononene have also been examined by the force-field calculations. Of its 10 minimum-energy conformations obtained, the asymmetric one which Favini *et al.* already studied has the lowest energy.

In the force-field calculations for (*Z*)-cyclononene (**2**), Favini *et al.* considered six conformations, *i.e.*, the chair-chair (CC), boat-chair (BC), chair-boat (CB), boat-boat (BB), twist chair-chair (TCC), and asymmetric (AS) conformation.[1] Since (*Z*)-2,3,4,7,8,9-hexahydrooxonin (**1**) can have the same molecular symmetry (C_S or C_2) as **2**, it may have conformations similar to those of **2**. We have recently carried out X-ray crystal structure analyses of two natural products, isolaurallene (**3**)[2] and neolaurallene (**4**),[3] and have found that the conformations of the nine-membered ether rings in **3** and **4** resemble each other, and that they differ essentially from any of the six conformations considered by Favini *et al.* It is of great interest to compare the stability of this new asymmetric (NAS) conformation with those of the other conformations. Thereupon, we have performed empirical force-field calculations for **1** and **2**. The present paper describes the X-ray structure determinations and molecular geometries of **3** and **4**, and discusses the results of the force-field calculations.



1



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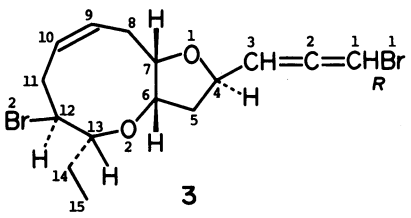

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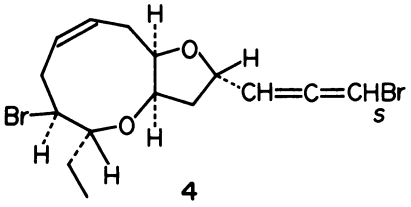

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Experimental

X-Ray Structure Determination of Isolaurallene (3). Colorless, needle-like crystals of **3** were kindly provided by Prof. E. Kurosawa. A single crystal cut into a cube with an edge of *ca.* 0.3 mm was used for the X-ray measurement. The crystal data were as follows: $C_{15}H_{20}O_2Br_2$, mol wt 392.13, orthorhombic, space group $P2_12_12_1$, a=10.393(2), b=27.824(4), c=5.397(1) Å, Z=4, D_c=1.669 g cm^{-3}, μ(Mo $K\alpha$)=51.4 cm^{-1}. The unit-cell dimensions and reflection intensities were obtained on a Rigaku four-circle diffractometer at the Ultra High Intensity X-Ray Diffraction Laboratory of Nagoya University, using graphite-monochromated Mo $K\alpha$ radiation (λ=0.71073 Å). The θ—2θ scanning mode was employed at a θ scan rate of 6° min^{-1}; the background was measured for 5 s at each end of the scan range. Three standard reflections, measured at intervals of every 200 reflections, showed no significant decrease in intensity during the course of data collection. The intensities were corrected for the Lorentz and polarization factors, but not for the absorption or the extinction effect. In the range of 2θ values up to 50°, 1091 unique structure factors above the $3\sigma(F)$ level were selected for the structure determination.

The structure was elucidated by the heavy-atom method, and refined by the block-diagonal least-squares method with anisotropic temperature factors. The absolute configuration was determined by Hamilton's method;[4] the R-factor ratio for the two enantiomeric structures, 1.045, excluded one of them at the 99.5% confidence level. After all the hydrogen atoms had been located in a difference Fourier map, further

least-squares refinements were carried out including the hydrogen atoms with the same fixed isotropic temperature factors of 4.5 Å^2. For these refinements, the following weighting scheme was used:

$$w = 1/\{\sigma(F)^2 \exp(c_1X^2+c_2Y^2+c_3XY+c_4X+c_5Y)\},$$

where $X=|F_o|$ and $Y=\sin\theta/\lambda$. The c_1, c_2, c_3, c_4, and c_5 coefficients were evaluated from the $(\Delta F)^2$ distribution; $c_1=0.237\times10^{-5}$, $c_2=-10.3$, $c_3=-0.877\times10^{-3}$, $c_4=0.142\times10^{-2}$, and $c_5=5.69$. The final R-value was 0.076. The atomic parameters thus obtained are listed in Table 1.[5] The bond distances and angles and the ring torsion angles are given in Table 2 and Fig. 1(a) respectively.

The calculations for the X-ray study were performed using our own programs. The atomic scattering factors and anomalous-dispersion corrections were taken from the International Tables.[6]

X-Ray Structure Determination of Neolaurallene (4). Colorless, needle-like crystals of **4** were also supplied by Prof. E. Kurosawa. The sample used for the X-ray experiment had dimensions of *ca.* 0.3×0.4×0.5 mm^3. The crystal data were as follows: $C_{15}H_{20}O_2Br_2$, mol wt 392.13, monoclinic, space group $P2_1$, $a=13.338(7)$, $b=4.929(1)$, $c=12.435(5)$ Å, $\beta=98.22(4)°$, $Z=2$, $D_c=1.609$ g cm^{-3}, μ(Mo $K\alpha$)=49.5 cm^{-1}. The cell dimensions and diffraction intensities were measured on a Rigaku four-circle diffractometer at the High Brilliance X-Ray Laboratory of Hokkaido University, using graphite monochromated Mo $K\alpha$ radiation (λ= 0.71073 Å). The θ—2θ scan teachnique was applied at a θ scan speed of 4° min^{-1}; the background was counted for 10 s at each end of the scan range. The intensities of three standard reflections, measured at intervals of every 100 reflections, decreased rapidly during the course of data collection; the final-intensity/initial-intensity ratios were *ca.* 0.56—0.68. The intensities were corrected for this damage to the sample as well as for the Lorentz and polarization factors, but not for the absorption or the extinction effect.

Table 1. The final atomic parameters and estimated standard deviations for isolaurallene (**3**)

Atom	10^3x	10^4y	10^3z	B_{eq}[a]/Å^2
Br (1)	154.9 (2)	288.6 (8)	11.5 (5)	5.9
Br (2)	839.5 (2)	1219.2 (7)	−123.8 (4)	4.2
O (1)	268 (1)	2033 (4)	479 (3)	5.0
O (2)	541 (1)	1328 (3)	367 (2)	2.5
C (1)	80 (2)	503 (8)	297 (5)	7.6
C (2)	90 (2)	971 (7)	364 (4)	4.0
C (3)	108 (2)	1415 (6)	427 (4)	4.2
C (4)	221 (2)	1600 (7)	571 (4)	4.6
C (5)	337 (2)	1272 (7)	575 (3)	4.6
C (6)	403 (2)	1396 (6)	337 (3)	2.4
C (7)	361 (2)	1928 (6)	287 (3)	3.3
C (8)	470 (2)	2310 (6)	313 (4)	4.1
C (9)	543 (2)	2342 (5)	71 (3)	3.1
C (10)	664 (2)	2180 (6)	35 (4)	4.2
C (11)	744 (1)	1911 (6)	226 (4)	3.5
C (12)	744 (1)	1351 (5)	175 (3)	2.6
C (13)	604 (1)	1168 (6)	151 (4)	3.4
C (14)	593 (2)	625 (6)	132 (4)	4.2
C (15)	657 (2)	360 (7)	347 (4)	5.7

a) $B_{eq}=8\pi^2(u_1^2+u_2^2+u_3^2)/3$, where u_i is the root-mean-square deviation in the i-th principal axis of the thermal ellipsoid.

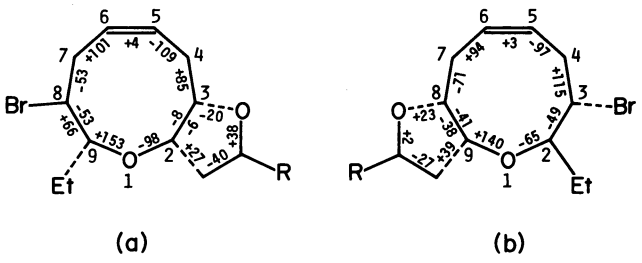

Fig. 1. The ring torsion angles (ϕ/°) in (a) isolaurallene (**3**) and (b) neolaurallene (**4**). The e.s.d.'s are 1—3°. For the sake of comparison, the numbering system for **1** is used.

Table 2. The bond distances (l/Å) and angles (θ/°) in isolaurallene (**3**)

C (1) - C (2)	1.36 (3)	C (12) - Br (2)	1.93 (2)	C (8) - C (7) - O (1)	107 (1)
C (1) - Br (1)	1.82 (2)	C (13) - C (14)	1.52 (2)	C (7) - C (8) - C (9)	109 (1)
C (2) - C (3)	1.29 (3)	C (13) - O (2)	1.41 (2)	C (8) - C (9) - C (10)	125 (2)
C (3) - C (4)	1.50 (3)	C (14) - C (15)	1.53 (3)	C (9) - C (10) - C (11)	125 (2)
C (4) - C (5)	1.51 (3)	C (2) - C (1) - Br (1)	121 (2)	C (10) - C (11) - C (12)	112 (1)
C (4) - O (1)	1.39 (2)	C (1) - C (2) - C (3)	176 (2)	C (11) - C (12) - C (13)	110 (1)
C (5) - C (6)	1.49 (2)	C (2) - C (3) - C (4)	125 (2)	C (11) - C (12) - Br (2)	110 (1)
C (6) - C (7)	1.57 (2)	C (3) - C (4) - C (5)	115 (2)	C (13) - C (12) - Br (2)	111 (1)
C (6) - O (2)	1.45 (2)	C (3) - C (4) - O (1)	113 (2)	C (12) - C (13) - C (14)	114 (1)
C (7) - C (8)	1.56 (2)	C (5) - C (4) - O (1)	104 (1)	C (12) - C (13) - O (2)	105 (1)
C (7) - O (1)	1.44 (2)	C (4) - C (5) - C (6)	103 (1)	C (14) - C (13) - O (2)	110 (1)
C (8) - C (9)	1.51 (3)	C (5) - C (6) - C (7)	104 (1)	C (13) - C (14) - C (15)	113 (2)
C (9) - C (10)	1.35 (3)	C (5) - C (6) - O (2)	109 (1)	C (4) - O (1) - C (7)	108 (1)
C (10) - C (11)	1.52 (3)	C (7) - C (6) - O (2)	115 (1)	C (6) - O (2) - C (13)	114 (1)
C (11) - C (12)	1.58 (2)	C (6) - C (7) - C (8)	115 (1)		
C (12) - C (13)	1.55 (2)	C (6) - C (7) - O (1)	105 (1)		

The e.s.d.'s given in parentheses refer to the last decimal position.

In the range of 2θ values up to 50°, 1002 independent structure factors above the $3\sigma(F)$ level were selected for the structure determination.

The structure was solved by the heavy-atom method. After the structure had been well refined by the block-diagonal least-squares method with anisotropic temperature factors, the absolute configuration was assigned by Bijvoet's method.[7] Twenty sets of hkl, $\bar{h}k\bar{l}$, $h\bar{k}l$, and $\bar{h}\bar{k}\bar{l}$ reflections having large values of $||F_c(hkl)|-|F_c(\bar{h}k\bar{l})||/\sigma(F)$[8] were selected for this purpose. The signs of the corresponding observed and calculated values of $\{|F(hkl)|+|F(\bar{h}k\bar{l})|-|F(h\bar{k}l)|-|F(\bar{h}\bar{k}\bar{l})|\}/2$ were in agreement with each other for all the 20 sets of reflections. The absolute configuration thus determined was supported also by the R-factor ratio for the two enantiomeric structures, 1.010.[4] Since a difference Fourier map revealed all the hydrogen atoms, further least-squares refinements were performed including the hydrogen atoms with the same fixed isotropic temperature factors of 5.7 Å^2. A weighting scheme similar to that for **3** was used; c_1=−0.107×10^{-2}, c_2=32.3, c_3=−0.144, c_4=0.160, and c_5=−29.4. In this manner, the R-value reached 0.069. The final atomic parameters are listed in Table 3.[5] The bond distances and angles and the ring torsion angles are given in Table 4 and Fig. 1(b), respectively.

Table 3. The final atomic parameters and estimated standard deviations for neolaurallene (**4**)

Atom	10^3x	10^3y	10^3z	B_{eq}[a]/Å^2
Br (1)	812.2 (2)	1095 (1)	279.1 (3)	12.1
Br (2)	77.8 (1)	244 (1)	440.4 (2)	5.9
O (1)	365.5 (7)	915 (3)	103.6 (9)	4.9
O (2)	279.1 (6)	720 (3)	293.0 (7)	3.6
C (1)	700 (1)	1208 (7)	188 (2)	8.0
C (2)	624 (1)	1038 (4)	160 (1)	5.3
C (3)	547 (1)	889 (4)	126 (1)	4.9
C (4)	454 (1)	861 (3)	184 (1)	2.9
C (5)	436 (1)	589 (3)	228 (1)	4.0
C (6)	322 (1)	558 (3)	214 (1)	3.1
C (7)	295 (1)	688 (3)	103 (1)	3.5
C (8)	190 (1)	800 (3)	74 (1)	4.7
C (9)	117 (1)	571 (4)	56 (1)	4.7
C (10)	64 (1)	461 (4)	130 (2)	6.1
C (11)	68 (1)	568 (4)	248 (2)	5.3
C (12)	144 (1)	402 (4)	324 (1)	3.6
C (13)	236 (1)	566 (3)	376 (1)	3.5
C (14)	317 (1)	407 (4)	448 (1)	4.2
C (15)	389 (1)	603 (5)	517 (1)	6.0

a) See Table 1.

Force-Field Calculations. The force-field calculations were performed using the MM2 program.[9] In the force-field calculations for **2**, Favini *et al.* assumed the C_S or C_2 symmetry for the whole or part of the molecule.[1] Since, however, there appeared to be no valid reason for having such symmetry, in our MM2 calculations, no symmetry was assumed for either **1** or **2**. As a result, it was found for **1** and **2** that, although the symmetric CB and BC conformations correspond to energy minima, the symmetric CC, BB, and TCC conformations correspond to energy maxima, and that, in order to reach energy minima, they must be considerably deformed. With respect to the plane which divides the molecule into two equal parts, the arrangements of the signs of the ring torsion angles in the CB, BC, CC, and BB minimum-energy conformations keep antisymmetric, while those in the AS, NAS, and TCC minimum-energy conformations are neither symmetric nor antisymmetric. Therefore, in this paper, the former four are still referred to as conformations CB, BC, CC, and BB, respectively, and the latter three are called conformations AS1, AS2, and AS3, respectively. In the course of the examination of the interconversions among the conformers of **1**, four additional minimum-energy conformations (AS4, AS5, AS6, and AS7) were obtained. As for **2**, a total of 10 minimum-energy conformations were found. Each of these conformations had the same arrangement of the signs of the ring torsion angles as the corresponding conformation of **1**. The AS6 conformation of **2** was found not to correspond to an energy minimum. When this conformation was optimized, it changed into a new minimum-energy conformation. However, because of the extremely-high strain energy (213

Table 4. The bond distances (l/Å) and angles (θ/°) in neolaurallene (**4**)

C (1) - C (2)	1.33 (3)	C (12) - Br (2)	1.96 (2)	C (8) - C (7) - O (1)	107 (1)
C (1) - Br (1)	1.83 (2)	C (13) - C (14)	1.52 (2)	C (7) - C (8) - C (9)	109 (1)
C (2) - C (3)	1.28 (2)	C (13) - O (2)	1.47 (2)	C (8) - C (9) - C (10)	127 (2)
C (3) - C (4)	1.52 (2)	C (14) - C (15)	1.54 (3)	C (9) - C (10) - C (11)	124 (2)
C (4) - C (5)	1.49 (2)	C (2) - C (1) - Br (1)	120 (2)	C (10) - C (11) - C (12)	109 (1)
C (4) - O (1)	1.45 (2)	C (1) - C (2) - C (3)	175 (2)	C (11) - C (12) - C (13)	114 (1)
C (5) - C (6)	1.51 (2)	C (2) - C (3) - C (4)	125 (2)	C (11) - C (12) - Br (2)	110 (1)
C (6) - C (7)	1.51 (2)	C (3) - C (4) - C (5)	116 (1)	C (13) - C (12) - Br (2)	108 (1)
C (6) - O (2)	1.45 (2)	C (3) - C (4) - O (1)	107 (1)	C (12) - C (13) - C (14)	116 (1)
C (7) - C (8)	1.50 (2)	C (5) - C (4) - O (1)	105 (1)	C (12) - C (13) - O (2)	110 (1)
C (7) - O (1)	1.46 (2)	C (4) - C (5) - C (6)	105 (1)	C (14) - C (13) - O (2)	111 (1)
C (8) - C (9)	1.49 (2)	C (5) - C (6) - C (7)	100 (1)	C (13) - C (14) - C (15)	110 (2)
C (9) - C (10)	1.35 (3)	C (5) - C (6) - O (2)	111 (1)	C (4) - O (1) - C (7)	109 (1)
C (10) - C (11)	1.55 (3)	C (7) - C (6) - O (2)	109 (1)	C (6) - O (2) - C (13)	115 (1)
C (11) - C (12)	1.52 (2)	C (6) - C (7) - C (8)	118 (1)		
C (12) - C (13)	1.54 (2)	C (6) - C (7) - O (1)	105 (1)		

The e.s.d.'s given in parentheses refer to the last decimal position.

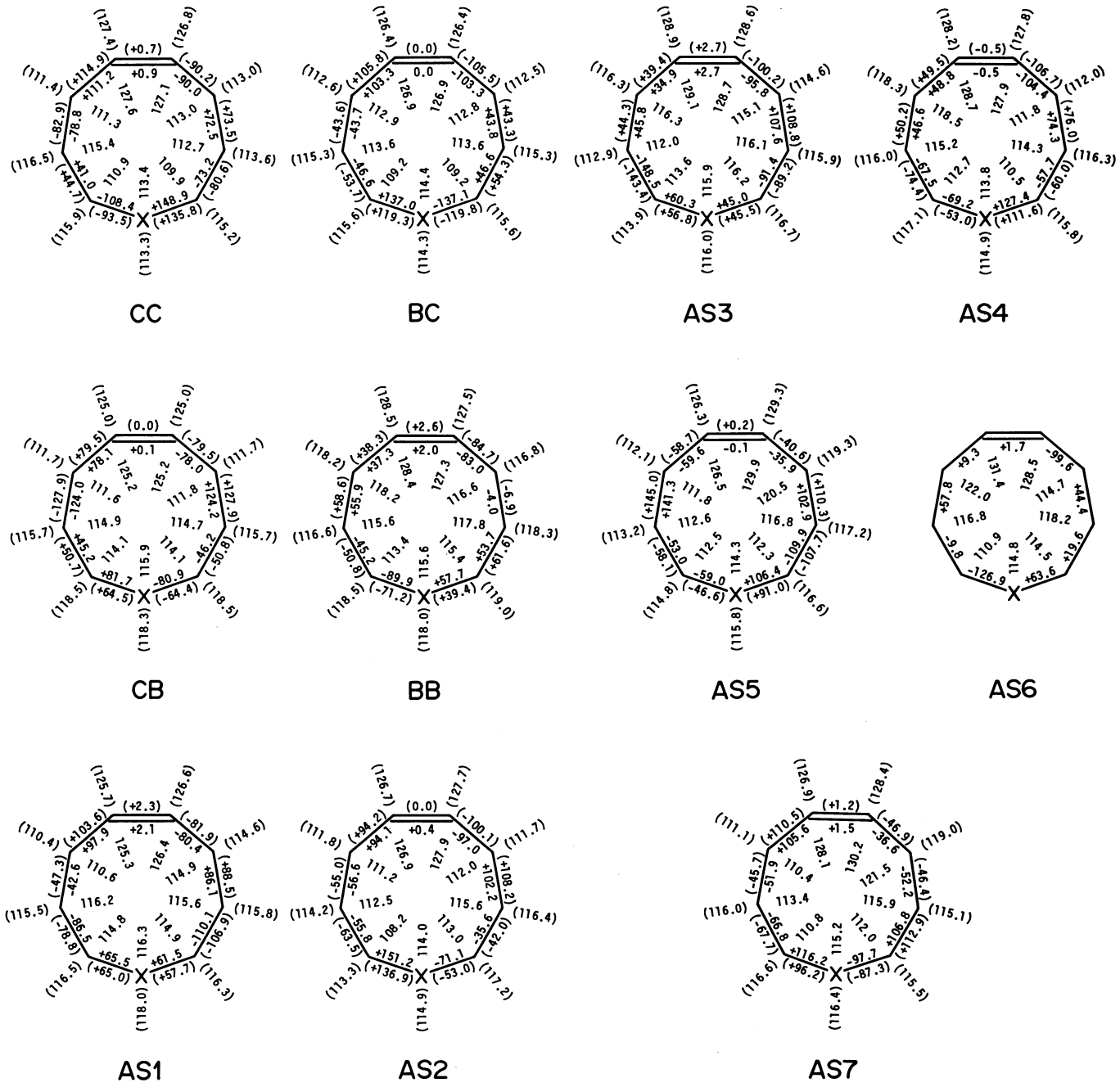

Fig. 2. The bond angles and ring torsion angles (ϕ/°) in (*Z*)-2,3,4,7,8,9-hexahydrooxonin (**1**, X=O) and (*Z*)-cyclononene (**2**, X=CH_2). The values for **2** are given in parentheses.

kJ mol^{-1} relative to AS1), this new conformation was not reckoned among minimum-energy conformations of **2**. The bond angles and ring torsion angles in the 11 different conformations are shown in Fig. 2.

Such interconversions among the conformers of **1** as could be accomplished by a change of one ring torsion angle were studied by the MM2 calculations. Each time the torsion angle used as a conversion parameter was changed by 5°, the strain energy of the molecule was minimized under the condition that this torsion angle should be fixed at the given value. From the energy profile thus obtained, the energy barrier to the conversion was estimated. The reversibility of the conversion was judged according to whether or not the energy change was continuous throughout the conversion. The results are summarized in Fig. 3.

Results and Discussion

(Z)-2,3,4,7,8,9-Hexahydrooxonin (1). The present study has revealed that there are at least 11 minimum-energy conformations of **1** (see Fig. 2). As can be seen from Table 5, the AS2 conformation is the most stable, and has a lower energy than the next most

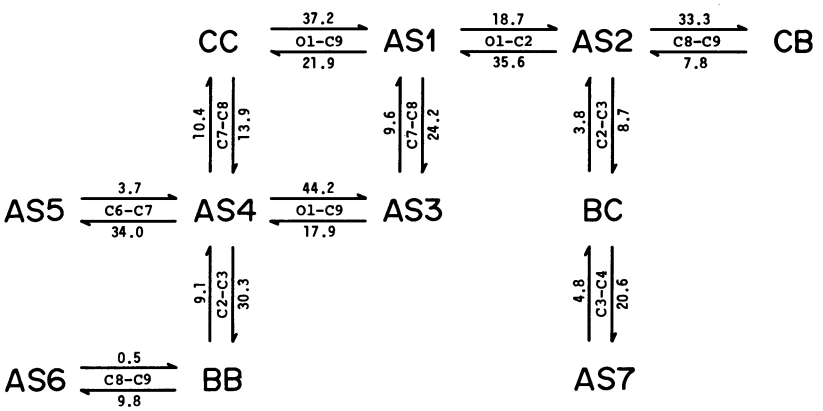

Fig. 3. The interconversions among the conformers of (Z)-2,3,4,7,8,9-hexahydrooxonin (**1**). The energy barriers (ΔE/(kJ mol^{-1})), together with the central bonds of the torsion angles used as conversion parameters, are shown.

stable CC conformation by 1.6 kJ mol^{-1}. The conformational interconversions for **1**, which can be accomplished by driving one ring torsion angle, are shown in Fig. 3. In addition to these reversible conversions, there are many irreversible conversions, *e.g.*, the AS5 →AS6→CC conversion caused by the rotation about the C8–C9 bond, the AS6→AS4 conversion caused by the rotation about the O1–C2, C2–C3, or C3–C4 bond, and the AS7→AS5*[10] conversion caused by the rotation about the C8–C9 bond. These irreversible conversions probably proceed reversibly, if they are performed by driving two or more ring torsion angles simultaneously. Accordingly, Fig. 3 should be considered to show only a part of the possible interconversions for **1**. The calculated energy barriers to the conversions shown in Fig. 3 are 44.2 kJ mol^{-1} or below, which suggests that, at room temperature, the conformations of **1** may change into one another directly or *via* one or more other conformations.

It is interesting to notice that the CB→AS2→BC transformation is accompanied by a remarkable change in torsional strain. Because of the eclipsed bond arrangements around the C7–C8 and C3–C4 bonds, the symmetric CB conformer has great torsional strains (11.6 kJ mol^{-1}) around these bonds (see Fig. 4). The changes from the CB to the AS2 conformer and from the AS2 to the BC conformer remarkably relieve these great torsional strains, respectively. However, the latter change results in an increase in the total strain energy. This is due mainly to the occurrence of great torsional strains around the O1–C2 and O1–C9 bonds.

Isolaurallene (3) and Neolaurallene (4). The conformations of the nine-membered rings in both **3** and **4** are substantially the same as the most stable AS2 conformation of **1** (see Figs. 1 and 2); the maximum torsion-angle deviations (28 and 15°) are observed for the junctures with the oxolane rings respectively. The diastereomeric compounds, **3** and **4**, have the same absolute configuration at each of

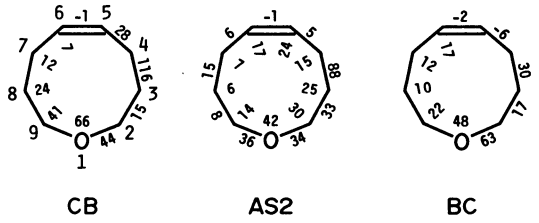

Fig. 4. The distributions of the torsional strain and bond-bending energies ($10\times E$/(kJ mol^{-1})) in the CB, AS2, and BC conformers of (Z)-2,3,4,7,8,9-hexahydrooxonin (**1**). The torsional energy ($E_t(i-j)$) and bending energy ($E_b(i)$), defined by the following equations, are shown for each bond and each atom respectively: $E_t(i-j)=\sum_{x,y} E_t(x-i-j-y)$; $E_b(i)=\sum_{x,y} E_b(x-i-y)$.

the carbon atoms to which the ethyl group or the bromine atom is attached, while they have different absolute configurations at each of the bridgehead carbon atoms. This stereochemical difference results in a striking contrast between **3** and **4** in regard to the positions of the substituents on the nine-membered ring having the asymmetric AS2 conformation. That is, in **3**, the oxolane ring is fused at the 2- and 3-positions, and the remaining substituents are placed at the 8- and 9-positions; the reverse is the case in **4**.

Since the calculated energy difference between the AS2 and CC conformations of **1** is only 1.6 kJ mol^{-1}, in order to explain why neither **3** nor **4** adopts the CC conformation, it is necessary to examine the steric effects of the substituents in some detail. In the CC conformation of **1**, the axial hydrogen atoms at the 2- and 9-positions are very close to each other, the distance being 2.17 Å (see Fig. 5). Therefore, the replacement of one of these hydrogen atoms by an alkyl group will make the CC conformation unstable. If the nine-membered ring in **4** takes the CC conformation, one of the ethyl and methylene groups attached

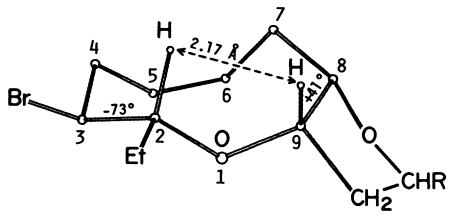

Fig. 5. The most probable arrangement of the substituents in the isolaurallene (**3**) molecule having the CC conformation.

to the C2 or C9 atom must necessarily be axial because of their trans configuration, which explains why **4** does not favor the CC conformation.

The explanation for **3** is not so easy as that for **4**. When **3** has the CC conformation, both of the ethyl and methylene groups bonded to the C2 or C9 atom will occupy the equatorial positions because of their cis configuration (see Fig. 5). If the cis fusion of the five- and nine-membered rings occurs at the C2 and C3 (or C8 and C9) atoms, the C-C2-C3-O (or O-C8-C9-C) torsion angle in the former ring should have almost the same value as the O1-C2-C3-C4 (or C7-C8-C9-O1) torsion angle. Since the magnitude of the C7-C8-C9-O1 torsion angle (41°) is much more suitable to the requirement of the oxolane ring than that of the O1-C2-C3-C4 torsion angle (−73°), it seems to be more reasonable to choose the C8-C9 bond as the junction of the two rings than to take the C2-C3 bond. In the former case, the ethyl group and the bromine atom are placed at the C2 and C3 atoms respectively. If it is assumed that the projections of the Et-C2-O1 and Br-C3-C4 bond angles along the C2-C3 bond are 120°, the Et-C2-C3-Br torsion angle is estimated to be about 47°. This value is somewhat smaller than the corresponding torsion angle (64°) in the AS2 conformation of **1** and the Et-C9-C8-Br torsion angle (66°) found actually in **3**, which would make the CC conformation of **3** more or less unstable. In the above explanation, the conformation of the oxolane ring in **3** has not been taken into consideration; for oxolane is known to be highly flexible.[11]

(Z)-Cyclononene (2). Although Favini *et al.* examined only six conformations of **2**, *i.e.*, the CC, BC, CB, BB, TCC, and AS conformations, the present study has shown that there are at least 10 minimum-energy conformations of **2** (see Fig. 2), and that the symmetric CC, BB, and TCC conformations correspond not to energy minima but to energy maxima. For the reason which has been mentioned in the preceding section, the minimum-energy conformations obtained by distorting the CC, BB, and TCC forms have been named CC, BB, and AS3 respectively, while the AS conformation has been renamed AS1. Table 5 indicates that the most stable conformation of **2** is AS1; this agrees with the result of Favini *et al.* The stability of the AS1 conformation is supported by the fact that the conformation found in the caprylolactam hydrochloride crystal resembles it closely.[12] However, the energy differences among the four most stable conformations of **2** are less than 4 kJ mol^{-1}; especially that between the AS1 and CC conformations is only 0.6 kJ mol^{-1}. This computational result suggests that substituted derivatives of **2** may have not the AS1 but the CC, AS2, or AS4 conformation according to the positions occupied by the substituents.

Table 5. The relative steric energies of the conformers of (*Z*)-2,3,4,7,8,9-hexahydrooxonin (**1**) and (*Z*)-cyclononene (**2**)

Conformer	*E*/(kJ mol^{-1})	
	1	**2**
CC	1.6	0.6
BC	4.9	4.4
CB	25.5	17.0
BB	26.3	22.3
AS1	16.8	0.0
AS2	0.0	2.3
AS3	31.4	14.3
AS4	5.1	2.4
AS5	35.4	27.5
AS6	35.6	
AS7	20.7	9.8

The absence of the AS6 minimum-energy conformation of **2** is explained as follows. In the AS6 conformation of **1**, the O1 atom is situated near the C4, C5, C6, and C7 atoms, the distances being 2.89, 2.92, 2.85, and 2.75 Å respectively. Therefore, when the O1 atom is replaced by a methylene group (-CH_2-), one of the hydrogen atoms in this methylene group must be very close to some of those four carbon atoms. This severe steric hindrance probably makes the AS6 conformation of **2** to be so labile as to be incapable of existing as a stable minimum-energy conformation.

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