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Studies on 5-8 Fused Ring Compounds. V. The Conformations of Eight-Membered Rings in 5-8-5 Fused Ring Compounds and Their cis-trans Isomerization

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The 5-8-5 fused ring compounds, synthesized by photocycloaddition, *cis-cisoid-cis-* and *cis-transoid-cis-*tricyclo[9.3.0.$0^{4,8}$]tetradecane-2,9-dione (**1-A** and **2-A**) and *cis-cisoid-cis*-tricyclo[9.3.0.$0^{3,7}$]tetradecane-2,9-dione (**3-A**) were isomerized to trans isomers (**1-B**, **1-C**, **2-B**, **2-C**, and **3-B**) at ring junction under basic conditions. Their molecular structures except for **1-B** were determined by X-ray crystallography. The eight-membered rings of these 5-8-5 fused ring compounds were found in various conformations, boat-chair, twist-boat (S_4), chair, twist-boat-chair, and chair-chair forms. With regard to the conformations of their eight-membered rings the strain energies were calculated by MM2 and the predicted conformations were compared with those obtained by X-ray crystallography.

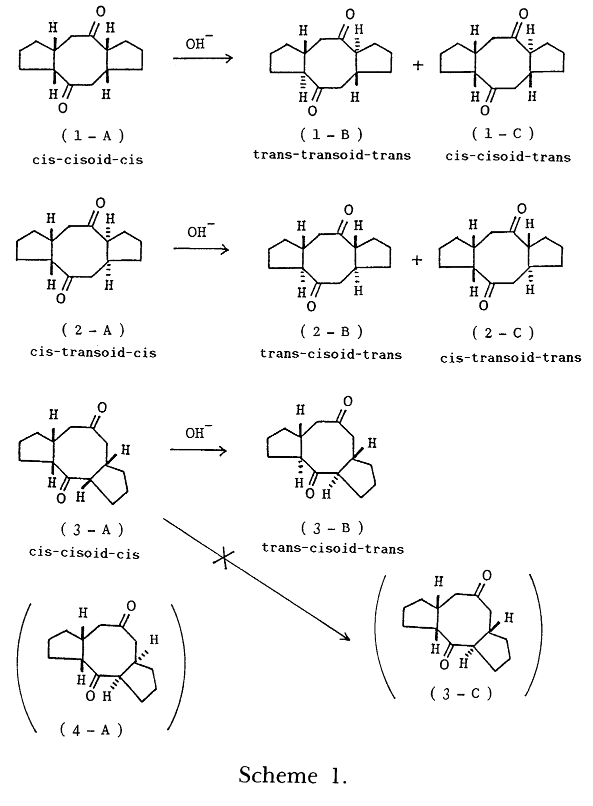
The cyclooctane ring is so flexible that there are many possible conformations which are designated by their symmetry. Although there have been a number of conformational studies on cyclooctane rings, little is known about the conformation on the 5-8-5 fused ring systems which are found amongst ophiobolins of sesterterpenes[1] and fusicoccin of diterpenes.[2] In order to provide the conformational information, we have synthesized 5-8-5 fused ring compounds and determined the molecular structures.

In the preceding paper[3,4] we reported the syntheses of 5-8-5 fused ring compounds by photocycloaddition and the molecular structures determined by X-ray crystallography. In this study several other cis-trans isomers at the ring junctions were synthesized and the molecular structures were determined by X-ray crystallography. Steric energies of these compounds were calculated by molecular mechanics (MM2 force field)[5] and the most stable conformations of their eight-membered rings were compared with the results of X-ray analyses.

Results and Discussion

The photoadducts, *cis-cisoid-cis-* and *cis-transoid-cis-*tricyclo[9.3.0.$0^{4,8}$]tetradecane-2,9-dione (**1-A** and **2-A**), and *cis-cisoid-cis*-tricyclo[9.3.0.$0^{3,7}$]tetradecane-2,9-dione (**3-A**) were synthesized by photochemical cycloaddition of bicyclo[4.3.0]nonane-2,4-dione to cyclopentene,[3] and their conformations were determined by X-ray crystallography,[4] as described previously. Among the possible four isomers, three isomers (**1-A**, **2-A**, and **3-A**) were isolated and one isomer (**4-A**) could not be detected. These compounds which have all cis configuration at ring junction, are isomerized to trans configuration under basic conditions. The compound **1-A** was isomerized to two isomers **1-B** and **1-C**, and **2-A** also gave two isomers **2-B** and **2-C**. On the other hand compound **3-A** gave only one isomer **3-B**,[4] and **3-C** could not be detected. Furthermore **1-C** and **2-C** were also isomerized to **1-B** and **2-B**, respectively (Scheme 1).

^{13}C NMR spectra of **1-C** and **2-C** show 14 peaks, corresponding to the 14 carbon atoms. However, **1-A**, **1-B**, **2-A**, **2-B**, **3-A**, and **3-B** gave ^{13}C NMR spectra



Scheme 1.

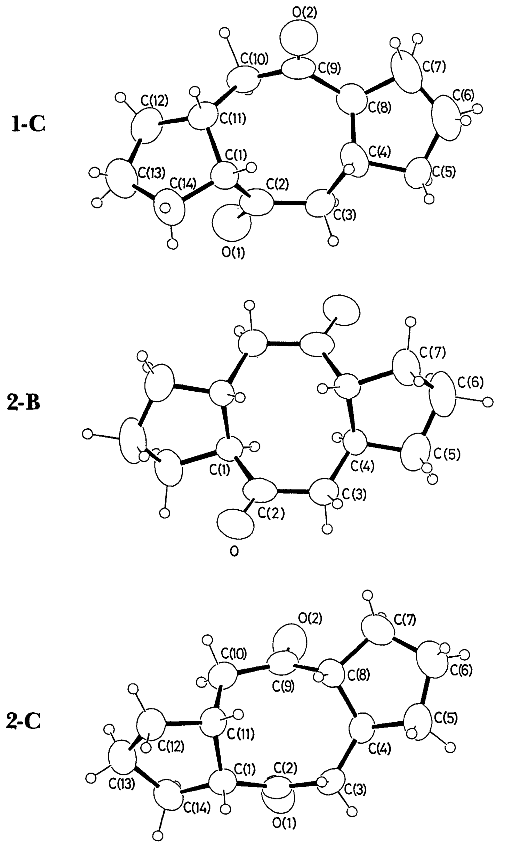


Fig. 1. Perspective views of the molecules **1-C**, **2-B**, and **2-C**.

consisting of only 7 peaks.[6] Therefore the formers are expected to exist in unsymmetrical structures and the latters are considered to take symmetric conformations. Consequently, it was assumed that **1-B**, **2-B**, and **3-B** are all trans at ring junctions, while in **1-C** and **2-C** one of the ring junction is cis and the other is trans.

The molecular structures of these compounds were determined by X-ray crystallography except for **1-B** of which suitable crystals were not available. The molecular structure of **3-B** was reported in a previous paper.[4] Figure 1 shows perspective views of **1-C**, **2-B**, and **2-C**. Figure 2 shows the side views of these 5-8-5 fused ring compounds, **1-A**, **1-C**, **2-A**, **2-B**, **2-C**, **3-A**, and **3-B**. The proposed cis-trans configurations of these compounds based on the ^{13}C NMR spectra agreed with the results of X-ray analyses. The cis-trans isomerization of **1-A** and **2-A** proceeds in the following pathway, **1-A**→**1-C**→**1-B** and **2-A**→**2-C**→**2-B**. In these 5-8-5 fused ring compounds, trans-fused isomers are more stable than the cis-fused isomers, as observed for the 5-8 fused ring compounds.[7]

Cyclooctane,[8] 1,5-cyclooctanedione,[9,10] and their simple derivatives[11] were found to be predominantly in boat-chair (BC) form, which is the most stable conformation predicted by the molecular mechanics calculations.[12–14] Previously we reported the molecular structures of two monobromo derivatives of 5-8 fused ring compounds and revealed that the eight-membered rings also take BC forms.[15] Since the strain energy difference between BC form and several other conformations is small, it has been expected that appropriately substituted derivatives of cyclooctane will possess conformations other than BC form. In this study, it was revealed that these 5-8-5 fused ring compounds actually exist in several different conformations, boat-chair (BC), twist-boat (S_4), chair (C), twist-boat-chair (TBC), and chair-chair (CC) forms.

The conformations of these compounds are shown in Table 1, and the observed (X-ray) and calculated (MM2) torsion angles for eight-membered rings in these compounds are compared in Table 1. The eight-membered rings in **2-C** and **3-A** exist in familiar BC form (BC-3,7), as in 1,5-cyclooctanedione. In Table 1, the deviation parameter ΔBC proposed by Miller et al.[10] is a measure of fit to the symmetrical BC conformation. Additionally, for the other conformations (C, S_4, TBC, and CC) we defined deviation parameters,[16] ΔC, ΔS_4, ΔTBC, and ΔCC and evaluated them (Table 1). The ΔBC values obtained from X-ray study for **2-C** and **3-A** are 19.9 and 20.3°, respectively. These values are larger than that for 1,5-cyclooctanedione (2.6°) and those from MM2 calculation (6.7 and 7.8°). The BC form of **2-C** and **3-A** in crystalline state may be strained by intermolecular interactions.

In **2-B** the eight-membered ring exists in chair (C) form as in **2-A** which shows a typical C form, though the eight-membered ring of **2-B** is somewhat twisted from C form. The ΔC values obtained from either X-ray study or MM2 for **2-B** (19.5 and 22.6°) are larger than those for **2-A** (2.5 and 2.9°). The position of five-membered ring fused to chair skeleton of eight-membered ring in **2-B** is different from that in **2-A** as seen from Fig. 2. The observed torsion angles (X-ray) in **2-A** and **2-B** are in excellent agreement with the calculated values (MM2).

The torsion angles of the eight-membered rings of **1-A**, **1-C**, and **3-B** which exist in conformations with S_4, TBC, and CC forms, respectively, are also listed in Table 1. In these compounds the observed torsion angles are in fairly good agreement with the calculated values.

The strain energies for the typical conformations of 1,5-cyclooctanedione and the 5-8-5 fused ring compounds were calculated. The former conformations and the strain energies were shown in Fig. 3 and those of the latter compounds were listed in Table 2. In Table 2, the strain energies of 5-8-5 fused ring compounds were calculated with the conformations corresponding to 1,5-cyclooctanedione with the lowest energy conformation, shown in Fig. 3. The strain energy for 1,5-cyclooctanedione indicates that BC-3,7 form is more stable than BC-1,5 form. However, BC-1,5 form was estimated as the most energetically

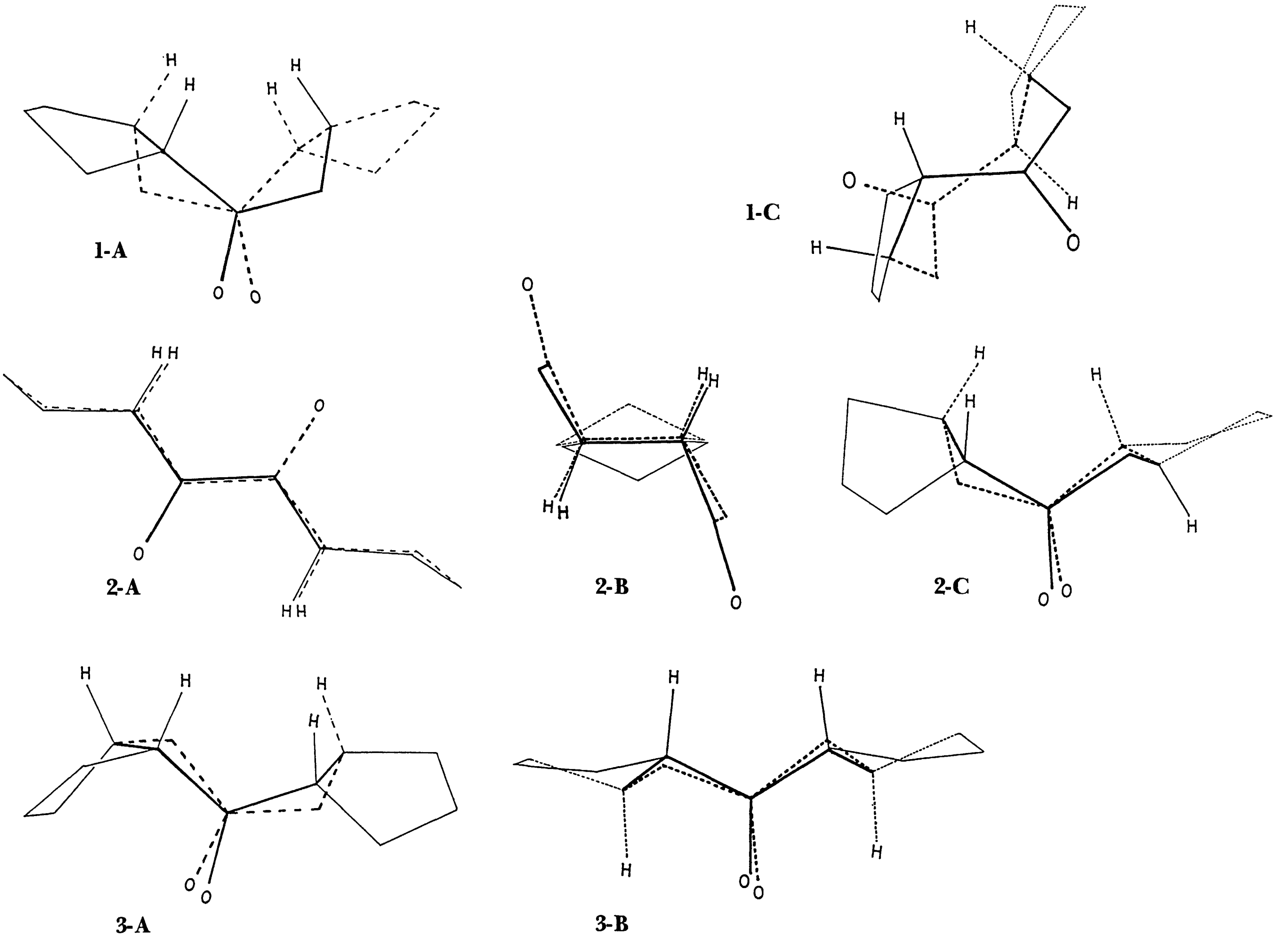


Fig. 2. The side views of the molecules **1-A**, **1-C**, **2-A**, **2-B**, **2-C**, **3-A**, and **3-B**.

favorable conformation for **3-B**. Furthermore for cyclooctane and 1,5-cyclooctanedione the C form is unfavorable because of high strain energy, and the structure with the C conformation has not hitherto been reported. Nevertheless, C form for **2-A** was calculated to be the lowest energy conformation and actually observed.

Thus it has become apparent that the stable conformations of the eight-membered rings in 5-8-5 fused ring compounds are different from that of cyclooctane or 1,5-cyclooctanedione.

The observed conformations of **1-A**, **1-C**, and **2-A** are consistent with the lowest energy. Therefore it may be assumed that their conformations in solution are for the most part the same as those in the solid state. On the other hand, for **2-B**, **2-C**, **3-A**, and **3-B** the conformations predicted by MM2 disagree with those obtained by X-ray analysis. The conformation of **1-B** was not determined by X-ray analysis, but the MM2 results show the CC form is the preferred conformation for the eight-membered ring in **1-B**. The strain energies for the isomers, **4-A** and **3-C** which could not be detected, are also calculated and listed in Table 2.

The strain energy of the observed conformation for **1-A** (S_4 form) is larger than that for **1-C** (TBC form), and for **3-A** (BC form) it is larger than that for **3-B** (CC form). These MM2 results are consistent with the above experimental results of isomerization under basic condition. However, for **2-A**, **2-B**, and **2-C** the MM2 results disagree with the experimental results because the strain energy of the observed conformation for **2-A** (C form) is smaller than those of **2-B** (C form) or **2-C** (BC form). Further investigation may be required with regard to these MM2 results.[17)]

In ^{1}H and ^{13}C NMR spectra,[6)] each carbon and proton was assigned on the basis of the two-dimensional proton–proton (^{1}H–^{1}H) and carbon–proton (^{13}C–^{1}H) correlation spectra. Table 3 shows the chemical shifts of the protons and carbons at ring junctions, which are α- and β-positions of the carbonyl groups. In the ^{1}H NMR spectra of these compounds, the chemical shifts of the protons at ring junctions which are β-positions of carbonyl group (H_β) appear in unusually low magnetic field. It seems to be attributed to the magnetic anisotropy of the carbonyl groups.[18)] The chemical shifts of the protons at ring junctions which are α- and β-positions of carbonyl group (H_α and H_β) show an appreciable

Table 1. Conformations and Torsion Angles (Calculated and Observed) for 8-Membered Rings

Conformations	Compounds		Torsion angles/°								Deviation parameters/°
			ω_1[a]	ω_2[a]	ω_3[a]	ω_4[a]	ω_5[a]	ω_6[a]	ω_7[a]	ω_8[a]	
Boat-chair (BC)	Cyclooctane	Calcd[b]	65.0	44.7	−102.2	65.0	−65.0	102.2	−44.7	−65.0	ΔBC[e]= 0.0
	1,5-Cyclooctanedione	X-Ray[c]	62.8	47.5	−107.5	69.2	−67.3	105.0	−50.1	−59.6	ΔBC[e]= 2.6
		MM2	60.3	50.3	−108.2	65.1	−65.3	108.1	−49.5	−60.8	ΔBC[e]= 0.4
	3-A	X-Ray[d]	68.4	31.3	−102.2	62.0	−48.8	104.3	−72.6	−43.9	ΔBC[e]=20.3
		MM2	59.3	48.0	−106.0	56.1	−50.8	103.4	−60.1	−52.4	ΔBC[e]= 6.7
	2-C	X-Ray	71.1	29.0	−100.3	70.3	−61.9	110.0	−66.5	−47.1	ΔBC[e]=19.9
		MM2	61.4	42.4	−104.9	69.4	−66.3	109.1	−57.4	−52.7	ΔBC[e]= 7.8
Chair (C)	Cyclooctane	Calcd[b]	119.9	−76.2	0.0	76.2	−119.9	76.2	0.0	−76.2	ΔC[f]= 0.0
	2-A	X-Ray[d]	125.3	−77.7	3.5	76.3	−125.3	77.7	−3.5	−76.3	ΔC[f]= 2.5
		MM2	122.9	−77.1	5.4	76.2	−123.5	76.3	−3.7	−77.1	ΔC[f]= 2.9
	2-B	X-Ray	114.1	−87.9	16.0	65.0	−114.1	87.9	−16.0	−65.0	ΔC[f]=19.5
		MM2	112.0	−89.3	18.3	61.8	−112.1	89.0	−17.6	−62.1	ΔC[f]=22.6
Twist-boat (S_4)	Cyclooctane	Calcd[b]	64.9	37.6	−64.9	−37.6	64.9	37.6	−64.9	−37.6	ΔS_4[g]= 0.0
	1,5-Cyclooctanedione	MM2	69.7	37.7	−59.9	−45.1	69.7	37.7	−59.9	−45.1	ΔS_4[g]= 8.6
	1-A	X-Ray[d]	74.5	26.8	−67.4	−33.4	74.5	26.8	−67.4	−33.4	ΔS_4[g]= 6.9
		MM2	77.1	24.3	−62.9	−35.8	77.1	24.3	−62.9	−35.7	ΔS_4[g]=12.8
Twist-boat-chair (TBC)	Cyclooctane	Calcd[b]	88.0	−93.2	51.9	44.8	−115.6	44.8	51.9	−93.2	ΔTBC[h]= 0.0
	1,5-Cyclooctanedione	MM2	93.4	−84.9	48.7	48.1	−120.3	44.8	48.9	−103.1	ΔTBC[h]= 7.2
	1-C	X-Ray	−78.4	80.2	−67.4	−25.5	100.8	−40.5	−61.3	105.9	ΔTBC[h]=15.6
		MM2	−81.9	94.0	−68.2	−20.0	108.2	−53.5	−54.0	92.1	ΔTBC[h]=16.5
Chair-chair (CC)	Cyclooctane	Calcd[b]	66.0	−105.2	105.2	−66.0	66.0	−105.2	105.2	−66.0	ΔCC[i]=0.0
	1,5-Cyclooctanedione	MM2	70.8	−105.9	104.4	−69.7	70.8	−105.9	104.4	−69.7	ΔCC[i]=1.3
	3-B	X-ray[d]	66.4	−100.7	108.7	−75.4	71.2	−98.8	103.8	−73.2	ΔCC[i]=6.0
		MM2	75.0	−100.3	102.4	−75.4	73.3	−96.6	99.6	−77.4	ΔCC[i]=2.8

a) The positions of the torsion angles ω_{1-8} are shown below.

	1-A	**1-C**	**2-A**	**2-B**	**2-C**		**3-A**	**3-B**
C(11)-C(1)-C(2)-C(3)	ω_1	ω_5	ω_8	ω_6	ω_7	C(11)-C(1)-C(2)-C(3)	ω_6	ω_7
C(1)-C(2)-C(3)-C(4)	ω_8	ω_4	ω_1	ω_7	ω_6	C(1)-C(2)-C(3)-C(7)	ω_7	ω_6
C(2)-C(3)-C(4)-C(8)	ω_7	ω_3	ω_2	ω_8	ω_5	C(2)-C(3)-C(7)-C(8)	ω_8	ω_5
C(3)-C(4)-C(8)-C(9)	ω_6	ω_2	ω_3	ω_1	ω_4	C(3)-C(7)-C(8)-C(9)	ω_1	ω_4
C(4)-C(8)-C(9)-C(10)	ω_5	ω_1	ω_4	ω_2	ω_3	C(7)-C(8)-C(9)-C(10)	ω_2	ω_3
C(8)-C(9)-C(10)-C(11)	ω_4	ω_8	ω_5	ω_3	ω_2	C(8)-C(9)-C(10)-C(11)	ω_3	ω_2
C(9)-C(10)-C(11)-C(1)	ω_3	ω_7	ω_6	ω_4	ω_1	C(9)-C(10)-C(11)-C(1)	ω_4	ω_1
C(10)-C(11)-C(1)-C(2)	ω_2	ω_6	ω_7	ω_5	ω_8	C(10)-C(11)-C(1)-C(2)	ω_5	ω_8

b) Ref. 12. c) Ref. 9. d) Ref. 4. e) $\Delta BC=(|\omega_1+\omega_8|+|\omega_2+\omega_7|+|\omega_3+\omega_6|+|\omega_4+\omega_5|)/4$. f) $\Delta C=(|\omega_1+\omega_5|+|\omega_2+\omega_4|+|\omega_6+\omega_8|+|\omega_3|+|\omega_7|)/4$. g) $\Delta S_4=(|\omega_1+\omega_3+\omega_5+\omega_7|+|\omega_2+\omega_4+\omega_6+\omega_8|)/4$. h) $\Delta TBC=(|\omega_2-\omega_8|+|\omega_3-\omega_7|+|\omega_4-\omega_6|)/3$. i) $\Delta CC=(|\omega_1+\omega_8|+|\omega_2+\omega_7|+|\omega_3+\omega_6|+|\omega_4+\omega_5|)/4$.

difference between cis- and trans-junctions. The protons of cis-junction appear comparatively at lower magnetic field than those of trans-junction. On the contrary to the chemical shifts of protons, the chemical shifts of trans-junction carbons appear at lower magnetic field than those of cis-junction carbons.

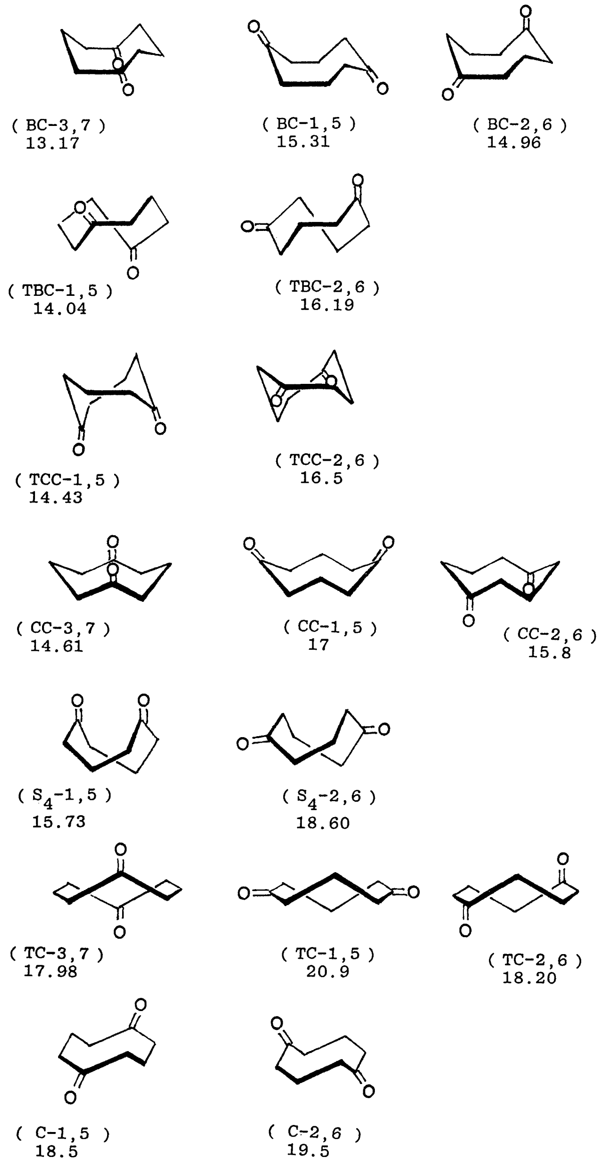


Fig. 3. Conformations and total energies of 1,5-cyclooctanedione by MM2. (kcal mol^{-1}). 1 kcal mol^{-1}=4.184 kJ mol^{-1}.

The 5-8-5 fused ring compounds exist in various conformations: BC, S_4, TBC, CC, and C forms as shown in Fig. 2. The variety of the conformations may be the result from the reduced flexibility of the eight-membered rings by the rigid five-membered rings fused to the eight-membered ring at two sites.

Experimental

Melting points are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-400 (400-MHz) spectrometer in $CDCl_3$ with TMS as the internal standard. The IR spectra were recorded using JASCO IR-G spectrometer. The mass spectra were obtained with a Hitachi M-80B mass spectrometer. The GC-analyses were carried out on a 263-50 Hitachi gas chromatography. Column chromatography was carried out with silica gel (Wakogel C-300).

Isomerization of 1-A to 1-B and 1-C. The compound **1-A**[3)] (0.3 g) was dissolved in a solution of potassium hydroxide(2 g)–water(10 ml)–ethanol (40 ml) and the solution was allowed to stand for 3 days at room temperature. The reaction mixture was neutralized with 1 M hydrochloric acid (1 M=1 mol dm^{-3}) and extracted with ether. The ethereal extract was washed with water and dried over sodium sulfate. Removal of the solvent under reduced pressure and the residue was subjected to silica-gel column chromatography. Elution with hexane–ether (2:1) gave *trans-transoid-trans*-tricyclo[9.3.0.0^{4,8}]tetradecane-2,9-dione (**1-B**) (143 mg) and crude *cis-cisoid-trans*-tricyclo[9.3.0.0^{4,8}]tetradecane-2,9-dione (**1-C**) which was further purified by column chromatography. (62 mg). In a GC-analysis of the reaction mixture, the ratio of **1-B** and **1-C** was approximately 1.8:1.

1-B: Mp 123—124 °C; IR (Nujol) 1690 cm^{-1} (C=O); MS *m/z* (rel intensity) 220 (M$^+$, 25), 192 (14), 178 (8), 165 (33), 153 (23), 152 (15), 137 (33), 124 (72), 111 (28), 95 (100, base), 83 (32), 81 (25), 67 (72), 55 (33), 41 (29). HRMS; Found: *m/z* 220.1459. Calcd for $C_{14}H_{20}O_2$: M, 220.1464. ^{1}H and ^{13}C NMR; (Ref. 6).

1-C: Mp 94—96 °C; IR (Nujol) 1700 and 1680 cm^{-1} (C=O); MS *m/z* (rel intensity) 220 (M$^+$, 71), 192 (8), 178 (13), 165 (50), 153 (57), 152 (27), 137 (39), 124 (100, base), 111 (33),

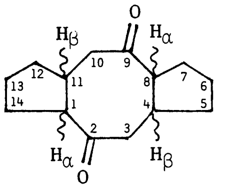
Table 2. Total Energies of **1-A**, **1-B**, **1-C**, **2-A**, **2-B**, **2-C**, **3-A**, **3-B**, **3-C**, and **4-A**/kcal mol^{-1}[a)] (by MM2)

Conformations	**1-A**	**1-B**	**1-C**	**2-A**	**2-B**	**2-C**	**3-A**	**3-B**	**3-C**	**4-A**
BC	36.40	—[e)]	36.13 (33.50)[c)]	38.07	33.77	34.00[b)] (32.84)[d)]	36.25[b)]	(31.45)[c)]	—	37.43
TBC	36.47	35.63	32.8[b)] (31.95)[d)]	34.60	32.76	35.82	34.70 (34.05)	34	34.71	36.92
TCC	39.1	33.76	36.34	38.88	—	36.34	40.92	—	37.41	41.7
CC	38.44	32.04	37.8	36.56	—	—	40.62	34.31[b)]	38	41.10
S_4	33.40[b)]	37.28	37.92	44.21	—	—	35.79	40.0	37.23	39.3
TC	37.61	—	37.6	46.9	—	—	38.5	45.42	39.95	38.1
C	36.78	—	—	32.54[b)]	34.12[b)]	43	—	—	37.83	38.01

a) 1 kcal mol^{-1}=4.184 kJ mol^{-1}. b) Observed conformation in crystals. c) BC-1,5 form. d) Asymmetric form. e) No energy minimum around the starting conformation.

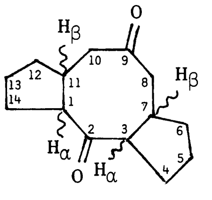
Table 3. Chemical Shifts of ^{1}H and ^{13}C NMR at Ring Junctions (α- and β-Positions of Carbonyl Groups)

Compounds (cis/cis)	Chemical shifts (δ/ppm)				Compounds (trans/trans)	Chemical shifts (δ/ppm)			
	α-Position		β-Position			α-Position		β-Position	
	^{13}C	^{1}H (H_α)	^{13}C	^{1}H (H_β)		^{13}C	^{1}H (H_α)	^{13}C	^{1}H (H_β)
1-A	52.48	3.33	36.84	3.09	**1-B**	57.34	3.00	47.86	2.13
2-A	55.25	3.10	40.41	2.91	**2-B**	56.75	2.58	42.04	2.35
3-A	54.80	3.07	42.78	2.62	**3-B**	59.04	2.77	46.50	2.16



1-A, 1-B

2-A, 2-B



3-A, 3-B

Table 4. Crystal Data, Experimental Conditions and Refinement Details

	1-C	2-B	2-C
Cell constants, *a* (Å)	10.448(2)	11.754(3)	18.895(3)
b	21.554(4)	5.457(2)	5.505(1)
c	5.398(1)	10.394(3)	12.125(2)
β (°)	90	115.16(2)	107.61(1)
V (Å^3)	1214.5(5)	603.4(3)	1202.1(3)
Space group	$P2_12_12_1$	$P2_1/n$	$P2_1/a$
Z	4	2	4
Size of specimen/mm^3	0.25X0.25X0.50	0.50X0.20X0.30	0.10X0.50X0.60
Range of *h*, *k*, and *l*	$0 \leqq h \leqq 12$ $0 \leqq k \leqq 25$ $0 \leqq l \leqq 6$	$-15 \leqq h \leqq 15$ $0 \leqq k \leqq 7$ $-13 \leqq l \leqq 13$	$-20 \leqq h \leqq 20$ $-5 \leqq k \leqq 0$ $0 \leqq l \leqq 13$
Number of reflections measured	1279	2767	1648
Number of reflections observed [$\lvert F_o \rvert > 3\sigma(\lvert F_o \rvert)$]	746	1135	1058
Transmission factor, *A*	0.975—0.987	0.978—0.986	0.967—0.993
Number of unique reflections	746	605	1006
Final *R* value	0.054	0.057	0.039
$(\Delta/\sigma)_{max}$ for nonhydrogen atoms	0.27	0.17	0.21
$\Delta\rho$/e Å^{-3})	−0.17, 0.14	−0.19, 0.36	−0.13, 0.15

95 (85), 83 (50), 81 (33), 67 (99), 55 (48), 41 (29). HRMS; Found: *m/z* 220.1453. ^{1}H and ^{13}C NMR; (Ref. 6).

Isomerization of 2-A to 2-B and 2-C. The compound **2-A**$^{3)}$ (0.2 g) was dissolved in a solution of potassum hydroxide (0.1 g)-ethanol(40 ml)-water(10 ml) and the solution was stirred for 1 h at room temperature. A similar work-up as mentioned above gave *trans-cisoid-trans*-tricyclo[9.3.0.0^{4,8}]-tetradecane-2,9-dione (**2-B**) (91 mg) and *cis-transoid-trans*-tricyclo[9.3.0.0^{4,8}]tetradecane-2,9-dione (**2-C**) (23 mg). The ratio **2-A**, **2-B**, and **2-C** was 1:3.2:1 by GC-analysis.

2-B: Mp 118—119 °C; IR (Nujol) 1688 cm^{-1} (C=O); MS *m/z* (rel intensity) 220 (M$^+$, 15), 192 (10), 178 (7), 165 (24), 153 (23), 152 (14), 137 (29), 124 (64), 111 (28), 95 (88), 83 (47), 81 (31), 67 (100, base), 55 (72), 41 (78). HRMS; Found: *m/z* 220.1468. Calcd for $C_{14}H_{20}O_2$: M, 220.1464. ^{1}H and ^{13}C NMR; (Ref. 6).

2-C: Mp 122—124 °C; IR (Nujol) 1685 and 1675 (sh) cm^{-1} (C=O); MS *m/z* (rel intensity) 220 (M$^+$, 18), 192 (5), 178 (4), 165 (18), 153 (21), 152 (10), 137 (19), 124 (52), 111 (22), 95 (62), 83 (35), 81 (29), 67 (100, base), 55 (60), 41 (78). HRMS; Found: *m/z* 220.1471. ^{1}H and ^{13}C NMR; (Ref. 6).

Isomerization of 1-C (or 2-C) to 1-B (or 2-B). The pure **1-C** (or **2-C**) (0.1 g) was dissolved in a solution of KOH (0.5 g)-EtOH(10 ml)-H_2O(3 ml) and the solution was allowed to stand for 24 h at room temperature. In a GC-analysis of the reaction mixture, the ratio of **1-B** and **1-C** was 2:1. (The ratio of **2-B** and **2-C** was 1:0.03)

Isomerization of 3-A to 3-B. The compound **3-A**$^{3)}$ (0.2 g) was dissolved in a solution of KOH (1 g)-EtOH (20 ml)-H_2O (5 ml) and the solution was allowed to stand for 2 days at room temperature. TLC (silica gel) analysis of the reaction mixture showes only one isomerization product. A similar work-up as mentioned above gave *trans-cisoid-trans*-tricyclo-[9.3.0.0^{3,7}]tetradecane-2,9-dione (**3-B**) (162 mg): Mp 120—

Table 5. Fractional Coordinates ($\times 10^4$) and Equivalent Thermal Parameters ($\times 10$)[a]

Atom	x	y	z	B_{eq}/Å$^2\times 10$
1-C				
O(1)	2283(4)	5601(2)	11271(7)	60
O(2)	595(4)	7245(2)	4512(8)	62
C(1)	2781(5)	6060(2)	7346(9)	34
C(2)	1929(5)	5710(2)	9177(9)	41
C(3)	614(5)	5496(2)	8380(10)	43
C(4)	−118(5)	5822(3)	6318(10)	42
C(5)	−1383(5)	5483(2)	5721(12)	52
C(6)	−2211(6)	5958(4)	4398(15)	84
C(7)	−1713(6)	6577(3)	5040(15)	79
C(8)	−579(5)	6483(2)	6800(10)	45
C(9)	485(5)	6965(2)	6446(10)	39
C(10)	1458(5)	7046(2)	8482(10)	42
C(11)	2757(5)	6768(2)	7832(9)	39
C(12)	3753(6)	6866(3)	9839(11)	55
C(13)	4780(6)	6376(3)	9354(13)	70
C(14)	4204(5)	5893(3)	7694(11)	55
2-B				
O(1)	3628(2)	611(5)	3256(3)	54
C(1)	4522(3)	4503(6)	3236(3)	33
C(2)	3861(3)	2672(6)	3747(4)	35
C(3)	3454(3)	3388(7)	4908(4)	40
C(4)	4009(3)	5651(7)	5792(3)	34
C(5)	3434(4)	6191(9)	6822(4)	56
C(6)	4465(4)	7438(11)	8108(4)	72
C(7)	5610(4)	6066(8)	8288(4)	49
2-C				
O(1)	2261(1)	3498(3)	1159(2)	51
O(2)	1546(1)	2632(4)	3573(2)	60
C(1)	3170(1)	531(5)	2057(3)	33
C(2)	2422(1)	1366(5)	1317(3)	33
C(3)	1850(1)	−579(5)	804(3)	36
C(4)	1220(1)	−616(5)	1340(3)	33
C(5)	627(2)	−2525(5)	819(3)	46
C(6)	213(2)	−2904(7)	1712(4)	61
C(7)	689(2)	−1751(6)	2822(4)	52
C(8)	1443(1)	−1181(5)	2640(4)	34
C(9)	1871(1)	861(5)	3364(4)	37
C(10)	2705(1)	742(5)	3843(4)	39
C(11)	3148(1)	−683(5)	3193(4)	34
C(12)	3975(1)	−732(6)	3885(5)	46
C(13)	4275(2)	1721(6)	3633(5)	51
C(14)	3770(2)	2482(6)	2437(5)	45

a) Ref. 23.

121 °C; IR (Nujol) 1688 and 1705 (sh) cm^{-1} (C=O); MS m/z (rel intensity) 220 (M$^+$, 4), 153 (14), 152 (25), 124 (100, base), 109 (7), 95 (93), 81 (55), 67 (97), 55 (40), 41 (77). HRMS; Found: m/z 220.1470. ^{1}H and ^{13}C NMR; (Ref. 6).

Crystal Structure Determination. The molecular structures of **1-C**, **2-B**, and **2-C** were determined by X-ray diffraction method. The chemical formula is $C_{14}H_{20}O_2$ with formula weight 220.3. D_x's are 1.21—1.22 Mg m^{-3} and μ (Mo K_α)'s are 0.073—0.074 mm^{-1}. Crystal data and experimental conditions are listed in Table 4. X-ray intensity measurements were performed on a Rigaku AFC-5 four-circle diffractometer with Mo K_α radiation (λ=0.71073 Å) monochromatized by a graphite plate. Five standard reflections showed no significant variation. Absorption correction was applied. The space group was uniquely determined from the Laue group and systematic absences. The structures were solved by a direct method with MULTAN 78,[19] and refined by block-diagonal least-squares with anisotropic thermal parameters for non-hydrogen atoms using UNICSIII computation program system.[20] Scattering factors were taken from International Tables for X-Ray Crystallography.[21] The numbers of H atoms located by difference synthesis were 14 among 20, 6 among 10, and 18 among 20 for **1-C**, **2-B**, and **2-C**, respectively. Positions of other H atoms were calculated and refined with isotropic thermal parameters. Final atomic parameters are listed in Table 5.[22] The molecule **2-B** has a center of symmetry.

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