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Studies on 5—8 Fused Ring Compounds. II. The Crystal and Molecular Structure of 7-Bromo-4,4-dimethylbicyclo[6.3.0]undecane-2,6-dione

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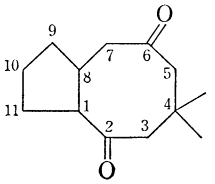
The crystal structure of 7-bromo-4,4-dimethylbicyclo[6.3.0]undecane-2,6-dione has been determined in order to elucidate the configuration and the conformation of 4,4-dimethylbicyclo[6.3.0]undecane-2,6-dione. The crystals of this compound are triclinic with space group $P\bar{1}$ and the unit cell dimensions are, $a=7.178$, $b=16.934$, $c=6.091$ Å, $\alpha=96.22$, $\beta=100.91$, $\gamma=115.39°$, and $Z=2$. The crystal structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method. The final R value for 1473 non-zero reflexions was 0.067. The ring fusion of this compound is *trans* and the 8-membered ring has a boat-chair conformation.

In a previous paper,[1)] it was reported that 4,4-dimethylbicyclo[6.3.0]undecane-2,6-dione (I) is given by the retro-aldol cleavage of 2-acetoxy-4,4-dimethyltricyclo[6.3.0.0^{2,7}]undecane-6-one which is the photoadduct of cyclopentene with the enol acetate of dimedone. This compound (I) has a fused ring system consisting of a five-membered ring and an eight-membered ring. No study concerning the conformations on such 5—8 fused ring compounds has been reported. Furthermore, no report concerning the relative stabilities of the *cis* and *trans* isomers of the 5—8 fused ring systems has appeared. Consequently the configuration of I at the ring juncture has not been assigned. In this work ^{1}H-NMR spectroscopy is not available for stereochemical study, because the ^{1}H-NMR spectra of I does not exhibit much difference in chemical shift and the definite assignment of each proton is not possible. In order to elucidate the conformation of I and to know whether the ring fusion is *cis* or *trans*, X-ray analysis of the monobromo derivative of I, 7-bromo-4,4-dimethylbicyclo[6.3.0]undecane-2,6-dione (II)[†,2)] has been conducted, because II forms more suitable crystals for X-ray analysis than I. Since II is easily debrominated[3)] by zinc dust in acetic acid at room temperature giving rise to the original dione (I), the ring fusion of I is probably the same as that of II.



(I)

Experimental

7-Bromo-4,4-dimethylbicyclo[6.3.0]undecane-2,6-dione (II) was synthesized by the bromination of I with pyridinium bromide perbromide in ethanol.[2)] Crystals of suitable quality for X-ray analysis were obtained from hexane in the form of colourless plates elongated along the b axis. The three-dimensional intensity data were collected on a Rigaku automatic four-circle diffractometer with graphite-monochromatized Cu $K\alpha$ radiation. The density was measured by the flotation method in a mixture of carbon tetrachloride and petroleum ether. The cell dimensions were determined by the least-squares method using the 2θ values of 20 strong reflexions in the range $36° \leq 2\theta \leq 50°$.

Crystal Data. 7-Bromo-4,4-dimethylbicyclo[6.3.0]undecane-2,6-dione, $C_{13}H_{19}O_2Br$, *F.W.* 287.2, mp 111—113 °C, triclinic, $a=7.178$ (3), $b=16.934$ (8), $c=6.091$ (3) Å, $\alpha=96.22$ (4), $\beta=100.91$ (3), $\gamma=115.39$ (4)°, $V=642$ Å^3, $D_m=1.49$ g/cm^3, $D_c=1.486$ g/cm^3, $Z=2$, space group $P\bar{1}$.

The three dimensional intensity data were collected with a $\omega/2\theta$ scan technique at a constant scanning rate of 2 deg/min. Reflexions having an intensity exceeding the corresponding standard deviations by three times were treated as observed. 1473 reflexions with $2\theta \leq 140°$ were retained and corrected for Lorentz and polarization factors but not for absorption and extinction factors.

Determination of the Structure

From the three dimensional Patterson map, the position of the bromine atom could easily be deduced. On the basis of the coordinates of the bromine atom, and from the Fourier synthesis all the 15 non-hydrogen light atoms in the asymmetric unit were deduced. The R-value was 0.52 at this stage. Refinement was conducted by the block-diagonal least-squares method. After several cycles of the refinement, the R-value was reduced to 0.295. Three cycles of calculations assuming the anisotropic thermal vibration for all the atoms gave an R-value of 0.098. From a second Fourier map, all hydrogen atoms except the five hydrogen atoms (H(5), H(8), H(11), H(13), and H(17)), were deduced. Three more cycles of refinement were performed using anisotropic temperature factors for the bromine, oxygen and carbon atoms and isotropic temperature factors for the hydrogen atoms. The final R-value for 1473 non-zero reflexions was 0.067. The scattering factors for bromine were taken from the International Tables for X-Ray Crystallography.[4)] For these calculations, computer programs made by Stewart *et al.*[5)] were used. The complete F_o-F_c tables are kept by the office of the Chemical Society of Japan (Document No. 7833).

The final values of the positional and thermal parameters are given in Tables 1 and 2. The molecular structure and the numbering of 7-bromo-4,4-dimethylbicyclo[6.3.0]undecane-2,6-dione (II) determined by the present analysis is shown in Fig. 1. Figure 2 shows

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[†] II was assumed to be the 5-bromo derivative in a previous paper,[2)] but this analysis showed it to be the 7-bromo derivative.

TABLE 1. FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) AND ANISOTROPIC THERMAL PARAMETERS ($\times 10^4$) OF THE NON-HYDROGEN ATOMS

The estimated standard deviations are given in parentheses. The anisotropic temperature factors are of the form: $\exp[-2\pi^2(a^{*2}h^2U_{11}+b^{*2}k^2U_{22}+c^{*2}l^2U_{33}+2a^*b^*hkU_{12}+2a^*c^*hlU_{13}+2b^*c^*klU_{23})]$.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br	1484(2)	4361(1)	765(2)	588(7)	569(7)	727(9)	390(6)	95(6)	65(7)
C(1)	4697(14)	2727(6)	387(16)	295(48)	485(57)	237(60)	233(45)	25(44)	47(51)
C(2)	3244(15)	1878(7)	−1142(17)	393(53)	624(68)	332(65)	403(54)	102(49)	97(58)
C(3)	1132(13)	1250(7)	−808(18)	258(44)	502(62)	442(69)	210(45)	47(45)	180(57)
C(4)	−879(14)	1257(7)	−2353(17)	244(45)	454(58)	351(62)	155(44)	24(44)	86(53)
C(5)	−810(14)	2183(7)	−1922(17)	270(46)	575(59)	390(65)	226(45)	135(46)	179(55)
C(6)	1018(14)	2944(7)	−2403(16)	333(48)	527(60)	312(58)	318(47)	92(44)	129(52)
C(7)	2763(16)	3639(7)	−557(17)	428(56)	486(61)	249(60)	281(52)	1(49)	−13(53)
C(8)	3684(14)	3299(6)	1391(16)	323(48)	493(58)	247(57)	278(46)	76(44)	21(51)
C(9)	5517(16)	4008(7)	3389(18)	431(57)	652(68)	392(67)	250(54)	−56(52)	16(59)
C(10)	6765(18)	3526(9)	4416(20)	590(68)	817(92)	261(74)	400(69)	−232(59)	−207(72)
C(11)	5913(16)	2608(8)	2645(18)	419(57)	744(79)	491(68)	435(60)	−28(51)	57(63)
C(12)	−1113(18)	946(8)	−4854(19)	504(68)	647(79)	400(69)	332(64)	46(57)	−47(64)
C(13)	−2823(16)	595(8)	−1657(22)	342(53)	601(71)	753(90)	171(52)	113(58)	224(69)
O(1)	3758(11)	1627(6)	−2847(14)	456(43)	859(61)	617(57)	395(44)	145(41)	18(50)
O(2)	1100(11)	2972(6)	−4387(12)	548(44)	801(56)	338(44)	303(43)	92(37)	189(44)

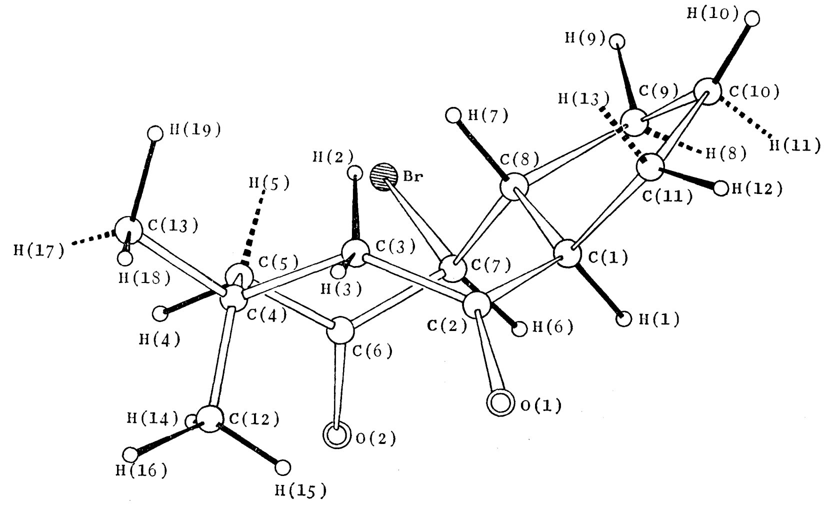


Fig. 1. Molecular structure and numbering of II. Projection of II along the b axis. (Hydrogen atoms connected with dot lines were not deduced.)

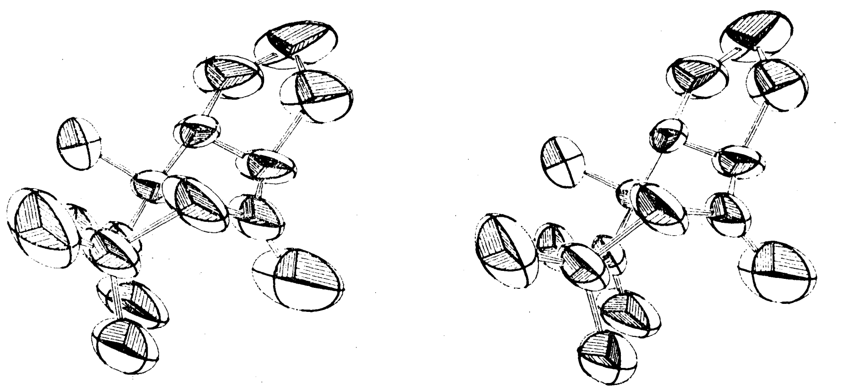


Fig. 2. A stereoscopic ORTEP drawing[6] of the molecule. Thermal ellipsoids are drawn at the 50% probability level.

TABLE 2. FRACTIONAL COORDINATES ($\times 10^3$) AND THERMAL PARAMETERS ($\times 10^2$) FOR HYDROGEN ATOMS
The estimated standard deviations are in parentheses.

	x	y	z	$U^{a)}$
H(1)	573(12)	303(5)	−61(14)	6(2)
H(2)	93(12)	137(5)	72(14)	7(2)
H(3)	78(12)	57(5)	−127(14)	3(2)
H(4)	−218(12)	207(5)	−308(14)	3(2)
H(6)	398(12)	412(5)	−133(14)	3(2)
H(7)	248(12)	294(5)	242(14)	4(2)
H(9)	510(12)	434(5)	483(14)	7(2)
H(10)	765(12)	369(5)	599(14)	9(2)
H(12)	709(12)	254(5)	254(14)	6(2)
H(14)	−132(12)	36(5)	−495(14)	7(2)
H(15)	27(12)	137(5)	−531(13)	7(2)
H(16)	−248(12)	87(5)	−596(14)	6(2)
H(18)	−284(12)	−3(5)	−221(14)	6(2)
H(19)	−260(12)	73(5)	21(14)	5(2)

a) U is defined by: $\exp(-8U\pi^2 \sin^2\theta/\lambda^2)$.

TABLE 3. BOND LENGTHS AND BOND ANGLES
Standard deviations are given in parentheses.

Bond lengths (l/Å)			
C(1)-C(2)	1.442(12)	C(10)-C(11)	1.589(17)
C(2)-C(3)	1.500(13)	C(11)-C(1)	1.566(16)
C(3)-C(4)	1.572(15)	C(1)-C(8)	1.576(17)
C(4)-C(5)	1.540(17)	C(4)-C(12)	1.510(15)
C(5)-C(6)	1.498(13)	C(4)-C(13)	1.539(15)
C(6)-C(7)	1.461(11)	C(2)-O(1)	1.257(15)
C(7)-C(8)	1.534(16)	C(6)-O(2)	1.226(13)
C(8)-C(9)	1.542(11)	C(7)-Br	2.004(13)
C(9)-C(10)	1.545(21)		
Bond angles (φ/°)			
C(1)-C(2)-C(3)	124.0(10)	C(11)-C(1)-C(8)	100.7(8)
C(2)-C(3)-C(4)	115.4(9)	C(11)-C(1)-C(2)	111.7(10)
C(3)-C(4)-C(5)	112.1(7)	C(1)-C(2)-O(1)	119.3(9)
C(4)-C(5)-C(6)	117.1(10)	C(3)-C(2)-O(1)	116.7(8)
C(5)-C(6)-C(7)	121.6(9)	C(3)-C(4)-C(12)	110.9(10)
C(6)-C(7)-C(8)	115.3(9)	C(3)-C(4)-C(13)	106.1(9)
C(7)-C(8)-C(1)	108.5(8)	C(5)-C(4)-C(12)	110.4(10)
C(8)-C(1)-C(2)	117.0(8)	C(5(-C(4)-C(13)	107.9(10)
C(1)-C(8)-C(9)	103.9(8)	C(12)-C(4)-C(13)	109.3(7)
C(7)-C(8)-C(9)	117.2(9)	C(5)-C(6)-O(2)	119.6(7)
C(8)-C(9)-C(10)	105.2(10)	C(7)-C(6)-O(2)	118.8(8)
C(9)-C(10)-C(11)	106.5(9)	C(6)-C(7)-Br	104.9(8)
C(10)-C(11)-C(1)	104.7(11)	C(8)-C(7)-Br	107.6(7)

the conformation and thermal vibration of the molecule drawn by the ORTEP.[6] The bond lengths and angles of the molecule, calculated from the coordinates given in Table 1, are shown in Table 3. Important torsion angles are shown in Table 4. The projection of the crystal structure along the c axis is shown in Fig. 3.

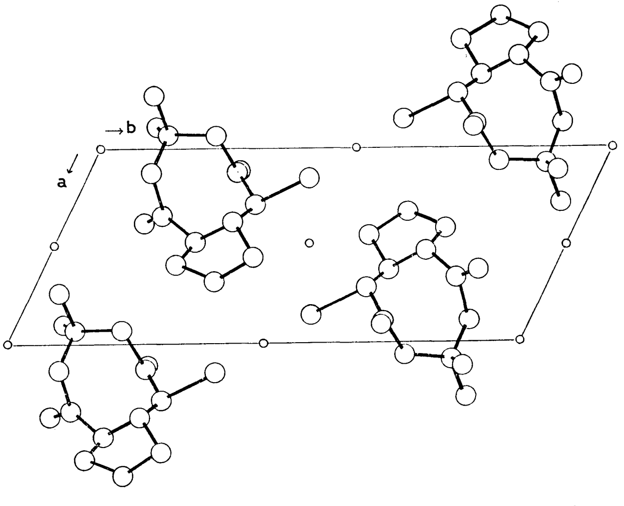
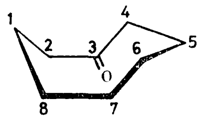


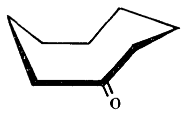
Fig. 3. Crystal structure projected along the c axis.

Discussion

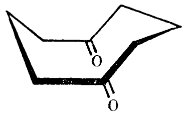
For the conformation of 8-membered rings, a boat-chair (BC) form was shown by the calculation of strain energies to be the most stable.[7] Cyclooctane and its simple derivatives have been found to be exist predominantly in the BC form,[8—10] however, since the energy differences from other conformations are small, the cases with crown family conformations (crown, chair-chair, and twist-chair-chair) are also reported.[10,11] For 8-membered ring ketones, Anet *et al.*[12] showed by NMR studies at low temperature that cyclooctanone and 1,5-cyclooctanedione exist in BC-3 (or BC-7) and BC-3,7 forms, respectively.



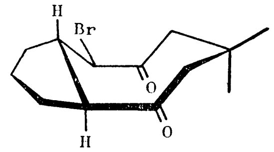
BC-3



BC-7



BC-3,7



(II)

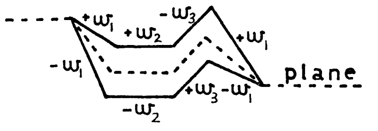
According to the results of this study, it has been shown that the 8-membered ring of II has a BC-3,7 conformation. In Table 5, the conformation of the 8-membered ring in II is shown in terms of torsion angles.[13] In these values, the torsion angles around the ring juncture and C(4) bearing two methyl groups, that is, C(8)–C(1), C(3)–C(4), and C(4)–C(5) deviated from the values of *cis*- and *trans*-1,2-cyclooctanedicarboxylic acids[8] and the calculated values for cyclooctane,[7] while the others are similar. When the 8-membered ring of II has a BC form, it is expected that the transannular repulsions occur between the three hydrogen atoms H(2), H(5), and H(7) which are directed towards the inside of the 8-membered ring. Although H(5) was not located the H(2)···H(7) interatomic distance was determined to be 2.4 Å. Since the interatomic distance is not small, these transannular interactions perhaps are weak, if any, in the crystalline

TABLE 4. TORSION ANGLES (φ/°)

Torsion angles in the 8-membered ring		Torsion angles in the 5-membered ring	
C(1)-C(2)-C(3)-C(4)	102.0	C(1)-C(8)-C(9)-C(10)	−35.0
C(2)-C(3)-C(4)-C(5)	−60.6	C(8)-C(9)-C(10)-C(11)	11.9
C(3)-C(4)-C(5)-C(6)	61.4	C(9)-C(10)-C(11)-C(1)	15.5
C(4)-C(5)-C(6)-C(7)	−107.1	C(10)-C(11)-C(1)-C(8)	−35.9
C(5)-C(6)-C(7)-C(8)	46.5	C(11)-C(1)-C(8)-C(9)	44.0
C(6)-C(7)-C(8)-C(1)	63.2		
C(7)-C(8)-C(1)-C(2)	−69.4		
C(8)-C(1)-C(2)-C(3)	−39.5		

Other torsion angles			
C(2)-C(1)-C(8)-C(9)	165.2	C(1)-C(8)-C(7)-Br	180.0
C(2)-C(1)-C(11)-C(10)	−160.8	C(5)-C(6)-C(7)-Br	−71.7
C(6)-C(7)-C(8)-C(9)	−179.5	C(9)-C(8)-C(7)-Br	−62.8
C(7)-C(8)-C(9)-C(10)	−154.6	O(1)-C(2)-C(1)-H(1)	15.8
C(7)-C(8)-C(1)-C(11)	169.4	O(1)-C(2)-C(3)-H(2)	163.6
C(2)-C(3)-C(4)-C(12)	63.5	O(1)-C(2)-C(3)-H(3)	36.6
C(2)-C(3)-C(4)-C(13)	−178.1	O(2)-C(6)-C(5)-H(4)	−43.0
C(6)-C(5)-C(4)-C(12)	−62.8	O(2)-C(6)-C(7)-H(6)	0.0
C(6)-C(5)-C(4)-C(13)	177.8	O(2)-C(6)-C(7)-Br	110.8
C(4)-C(3)-C(2)-O(1)	−79.3	H(1)-C(1)-C(8)-H(7)	177.2
C(4)-C(5)-C(6)-O(2)	70.3	H(6)-C(7)-C(8)-H(7)	167.0
C(8)-C(1)-C(2)-O(1)	141.8	H(7)-C(8)-C(7)-Br	51.6
C(8)-C(7)-C(6)-O(2)	−131.0		

TABLE 5. CONFORMATIONS FOR 8-MEMBERED RINGS IN TERMS OF TORSION ANGLES AROUND CARBON FRAMEWORK[13)]
According to the accepted notation, the axis or plane of symmetry is represented by a horizontal symmetry line.

	$+\omega_1$ $-\omega_1$	$+\omega_2$ $-\omega_2$	$-\omega_3$ $+\omega_3$	$+\omega_1$ $-\omega_1$
Compound II	63.2	46.5	−107.1	61.4
	−69.4	−39.5	102.0	−60.6
cis-1,2-Cyclooctanedicarboxylic acid[8)]	68.8	38.0	−96.1	65.7
	−60.1	−48.2	104.8	−67.4
trans-1,2-Cyclooctanedicarboxylic acid[8)]	63.0	43.4	−100.9	70.3
	−62.0	−46.8	105.9	−70.8
Cyclooctane, BC form (calculated by Englar *et al.*[7)])	64.0	43.4	−101.1	68.1
	−65.0	−41.9	100.3	−68.3
Cyclooctane, BC form (calculated by Hendrickson[7)])	65.0	44.7	−102.2	65.0
	−65.0	−44.7	102.2	−65.0

state.

The C–C–C bond angles in the 8-membered ring at C(1), C(3), C(5), and C(7) which are at α-positions of the carbonyl groups are 115—117 °C. Although these values are larger than the normal values of 109.5°, they are similar to the values observed in the 8-membered ring of 1,2-cyclooctanedicarboxylic acid.[8)] As shown in Table 3, the four C–C bond lengths containing carbonyl carbon atoms (C(2) and C(6)) are C(1)–C(2)=1.442 Å, C(2)–C(3)=1.500 Å, C(5)–C(6)=1.498 Å, and C(6)–C(7)=1.461 Å, respectively. In these values, the C(1)–C(2) bond length is significantly shorter than that for the usual C_{sp^2}–C_{sp^3} single bond (1.501 Å).[14)] The value of the C(2)–O(1) bond length s 1.257 Å which is longer than the characteristic value for the C=O double bond length. In the 8-membered ring, the distance between the two carbonyl carbon atoms, C(2)···C(6) is 2.951 Å and this is considerably shorter than the other distances between two carbon atoms in the 1,5 positions: C(1)···C(5)=3.598 Å, C(3)···C(7)=3.673 Å, C(4)···C(8)=3.693 Å.

The ring fusion of the 5-membered ring and the 8-membered ring in II is *trans* because the torsion angle H(1)–C(1)–C(8)–H(7) is 177.2° as shown in Table 5. Therefore the ring fusion of I may be assumed to be *trans*.

As shown in Figs. 1 and 2, the bromine atom in II was found to be bonded to C(7) in disagreement with what was assumed in a previous paper,2) *i.e.* bromine substitution at C(5). Also in a previous paper2) it was reported that the C=O at position 6 and C–Br in II greatly deviated from co-planarity on the basis of IR and UV data. This is consistent with the result of this study because the torsion angle O(2)–C(6)–C(7)–Br is 110.8°, whereas the torsion angle O(2)–C(6)–C(7)–H(6) is 0.0°.

Thus the 8-membered ring of II has a BC-3,7 conformation which appears to be the most stable. Consequently it may be assumed that I has a similar conformation.

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