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The Crystal Structure of *dl*-1,1,4aα-Trimethyl-2α-hydroxy-8β-methoxy-1,2,3,4,4a,5,6,7,8,9-decahydrophenanthrene

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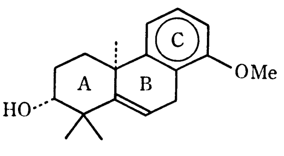
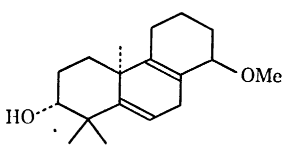
The crystal structure of the title compound has been determined from three-dimensional data collected on an automatic, four-circle diffractometer. The racemic crystals are triclinic, with two molecules in a unit cell of these dimensions; $a=10.502$, $b=11.706$, $c=7.488$ Å, $\alpha=71°33'$, $\beta=91°46'$, and $\gamma=116°22'$. The space group is $P\bar{1}$. The structure was solved by the symbolic addition method and was then refined by the block-diagonal-matrix least-squares method, with isotropic temperature factors for the hydrogen atoms and with anisotropic ones for the others. The final R value was 6.7%. The length of the C–C single bond opposite to the double bond in the cyclohexene ring is only 1.34 ± 0.01 Å. This apparent remarkable shortening can be well explained on the assumption that the two atoms concerned vibrate vigorously with parallel and antiparallel harmonic components perpendicular to the plane of the ring. It is shown that, if the root-mean-square amplitudes of the former components are taken to be equal to that of the thermal vibration of the carbon atom adjacent to one of the two atoms, the above C–C distance, corrected for these antiparallel motions, becomes quite reasonable: 1.60 Å.

It has recently been reported that the Birch reduction of 1,1,4aα-trimethyl-2α-hydroxy-8-methoxy-1,2,3,4,4a,9-hexahydrophenanthrene, I, produced an unexpected product, II.[1] The X-ray study of the *p*-bromobenzoate of II has revealed that the C ring of cyclohexene-type shows an unusual thermal behavior in the crystalline state.[2] In order to obtain more accurate information about the behavior of the C ring, an X-ray crystallographic analysis of II itself has now been carried out.



I



II

Experimental

Colorless, single crystals of II (racemate), $C_{18}H_{28}O_2$ (mp 162—164 °C), were obtained from a chloroform solution. A crystal with dimensions of about $0.2\times0.3\times0.4$ mm was used for the X-ray measurement. The crystal data are summarized in Table 1. The cell dimensions were measured by using a single-crystal diffractometer with Cu$K\alpha$ radiation ($\lambda=1.54178$ Å). The space group was assumed to be $P\bar{1}$ at the beginning of the study; this choice was later confirmed by a successful refinement. The intensity data were collected on an automatic, four-circle diffractometer at this University, using Cu$K\alpha$ radiation monochromatized with a LiF crystal. The intensity measurement was made by using an ω-2θ continuous scan at a rate of about $0.5°(\omega)$/min; the background was measured for 30—60 s at each end of the scan range. The intensities thus obtained were corrected for the Lorentz and polarization factors, but not for either the absorption or the extinction effect. In all, out of the structure factors of reflections with 2θ values up to 140°, 2276 above $3\sigma(F)$ were selected for the structural study.

Table 1. The crystal data

Crystal system Space group	Triclinic $P\bar{1}$
a	10.502 ± 0.002 Å
b	11.706 ± 0.003
c	7.488 ± 0.002
α	$71°33'\pm2'$
β	$91°46'\pm3'$
γ	$116°22'\pm2'$
Z	2
D_x	1.183 g/cm³

Structure Determination

The structure was solved by the direct method on the basis of 511 $|E|$ values above 1.30.[3] The origin was specified by assigning positive signs to three linearly-independent reflections, as is shown in Table 2. At the early stage of the structure determination, the symbolic addition procedure was carried out by the use of three symbols, *A*, *B*, and *C*. However, this procedure turned out to be unsuccessful, for no *E*-maps calculated from the eight possible combinations of the numerical values of the symbols afforded an acceptable structure. This difficulty was overcome by adding a fourth symbol, *D*. The correct combination of the values of the symbols, $A=B=C=\pi$ and $D=0$, was chosen by the method that had been used in the structure determination of the acetolysis product of II.[4] An *E*-map calculated with 461 phases clearly revealed the positions of all twenty non-hydrogen atoms. The structure thus obtained was refined at first by the block-diagonal-matrix least-squares method with isotropic temperature factors. After it had been ascertained that there was no other remarkable peak in a Fourier diagram, the structure was further refined by the

Table 2. The starting set

h	k	l	$\|E\|$	φ
2	7	3	4.73	0
$\bar{8}$	1	2	4.54	0
$\bar{3}$	4	6	4.10	0
4	10	4	5.00	*A*
$\bar{8}$	1	1	4.30	*B*
$\bar{2}$	2	0	3.26	*C*
9	0	4	3.96	*D*

TABLE 3. THE FINAL ATOMIC PARAMETERS WITH THEIR STANDARD DEVIATIONS

(a) The non-hydrogen atoms

The parameters are multiplied by 10^4.

(1) The fractional coordinates

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
O(1)	7614(2)	3884(2)	2840(4)	C(9)	2049(3)	−455(2)	3124(3)
O(2)	54(2)	−3306(2)	6912(4)	C(10)	3300(2)	987(2)	2556(3)
C(1)	4636(3)	1006(3)	1695(4)	C(11)	1763(4)	−1146(4)	1637(5)
C(2)	5988(3)	2344(3)	1338(4)	C(12)	560(6)	−2519(6)	2233(9)
C(3)	6330(3)	2656(3)	3166(4)	C(13)	−480(8)	−2948(6)	3641(8)
C(4)	5115(3)	2772(2)	4069(3)	C(14)	−139(3)	−2411(3)	5248(4)
C(5)	3686(2)	1494(2)	4256(3)	C(15)	5499(3)	2903(3)	6021(5)
C(6)	2812(3)	833(2)	5878(3)	C(16)	5044(3)	4088(3)	2903(5)
C(7)	1435(3)	−423(3)	6264(4)	C(17)	2804(3)	1898(3)	1032(4)
C(8)	1192(3)	−1056(2)	4762(3)	C(18)	−1218(3)	−4389(3)	8017(5)

(2) The anisotropic temperature factors

These are expressed as

$$\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{23}kl+\beta_{31}lh)\right].$$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{31}
O(1)	86(2)	104(2)	338(6)	41(3)	−102(6)	−15(5)
O(2)	88(2)	94(2)	357(6)	42(3)	4(6)	−19(6)
C(1)	117(3)	101(3)	188(5)	82(5)	−115(6)	32(6)
C(2)	107(3)	110(3)	210(6)	70(5)	−81(6)	70(7)
C(3)	89(3)	80(2)	224(5)	67(4)	−55(6)	−24(6)
C(4)	92(3)	74(2)	171(5)	53(4)	−79(5)	−28(5)
C(5)	90(2)	70(2)	145(4)	71(4)	−77(5)	−33(5)
C(6)	101(3)	93(2)	145(4)	64(4)	−111(5)	−28(5)
C(7)	102(3)	103(3)	153(5)	39(4)	−89(6)	27(6)
C(8)	91(2)	80(2)	166(4)	54(4)	−83(5)	−38(5)
C(9)	105(3)	91(2)	146(4)	75(4)	−108(5)	−52(5)
C(10)	98(3)	78(2)	123(4)	71(4)	−59(5)	−16(5)
C(11)	165(4)	128(3)	223(6)	32(6)	−209(8)	−1(8)
C(12)	241(8)	224(7)	450(14)	−116(13)	−506(19)	153(18)
C(13)	336(12)	208(7)	379(13)	−266(16)	−374(17)	192(20)
C(14)	103(3)	94(3)	211(5)	38(5)	−86(6)	−41(6)
C(15)	124(3)	108(3)	227(6)	42(5)	−160(7)	−73(7)
C(16)	129(3)	87(3)	288(7)	92(5)	−99(7)	−54(8)
C(17)	134(3)	107(3)	169(5)	112(5)	−67(6)	−65(6)
C(18)	117(3)	103(3)	302(8)	45(5)	−34(8)	10(8)

(b) The hydrogen atoms

The positional and thermal parameters are multiplied by 10^3 and 10 respectively.

Atom	x/a	y/b	z/c	B(Å^2)	Atom	x/a	y/b	z/c	B(Å^2)
H(1–1)	476(4)	28(3)	255(5)	19(6)	H(15–1)	547(5)	203(4)	688(6)	34(8)
H(1–2)	446(4)	83(4)	57(5)	23(6)	H(15–2)	640(4)	361(4)	586(6)	30(7)
H(2–1)	680(4)	226(4)	83(5)	24(6)	H(15–3)	487(5)	308(5)	663(7)	43(9)
H(2–2)	587(5)	301(4)	50(6)	31(7)	H(16–1)	421(5)	410(5)	345(7)	37(8)
H(3)	643(3)	192(3)	404(4)	9(5)	H(16–2)	597(5)	486(5)	303(7)	42(9)
H(6)	309(3)	123(3)	693(5)	16(5)	H(16–3)	510(6)	418(6)	164(9)	56(12)
H(7–1)	70(5)	−19(4)	642(6)	33(8)	H(17–1)	349(5)	277(5)	42(7)	42(9)
H(7–2)	139(4)	−104(4)	741(5)	27(7)	H(17–2)	206(5)	202(5)	151(7)	46(10)
H(11–1)	159(8)	−54(8)	46(11)	79(17)	H(17–3)	249(5)	155(5)	11(7)	41(9)
H(11–2)	255(6)	−97(6)	104(8)	49(11)	H(18–1)	−94(6)	−491(6)	911(8)	48(11)
H(12–1)	42(5)	−293(5)	134(7)	44(10)	H(18–2)	−183(7)	−479(6)	727(9)	58(12)
H(13–1)	−118(7)	−354(6)	389(9)	56(12)	H(18–3)	−183(9)	−415(8)	883(12)	80(17)
H(14)	−98(4)	−231(4)	568(5)	26(7)	H(O)	832(6)	366(5)	292(8)	47(10)

least-squares method, anisotropic thermal motions being assumed for all the non-hydrogen atoms. In this way, the discrepancy factor, R, was reduced to 11.9%. Out of the twenty-eight hydrogen atoms in the molecule, twenty-six were located in a difference Fourier map. The least-squares refinement was further repeated including these hydrogen atoms. In this refinement, the following weighting scheme was used:

$$W = 1/\{\sigma(F_o)^2 \exp(AX^2+BY^2+CXY+DX+EY)\},$$

where $X=|F_o|$ and $Y=\sin\theta/\lambda$.[4] The intensity data were grouped with constant intervals along two coordinates, $|F_o|$ and $\sin\theta/\lambda$. The coefficients, A, B, C, D, and E, were determined by the least-squares fit so as to give as equal values of $\langle W|\Delta F|^2\rangle$ for all the groups as possible. The final R value was 6.7%. The atomic parameters thus obtained are listed in Table 3.

The calculations for the present study were performed on a FACOM 230-60 computer at the Computer Center of Hokkaido University, using our own programs. The atomic scattering factors were taken from International Tables for X-ray Crystallography (1962), Vol. III. The tables of the observed and calculated structure factors are preserved by the Chemical Society of Japan (Document No. 7408).

Results and Discussion

The molecular framework of II and the torsion angles for the tricyclic system are given in Figs. 1 and 2 respectively. The molecular conformation of II is found to resemble closely that of its *p*-bromobenzoate derivative, hereafter called III;[2] the A and B rings take a distorted chair- and a somewhat flattened boat-form respectively, while the C ring has a considerably flattened half-chair conformation, with the methoxyl group oriented axially. A closer examination of the torsion angles shows that the conformational differences between the corresponding A, B, and C rings of II and III become greater in that order. This seems strange at first sight, since II differs from III simply in having a free hydroxyl group instead of a *p*-bromobenzoyloxy group in the A ring. However, this might be explained in terms of the theory that the unstable and flexible conformation of the C ring is more or less influenced by the hydrogen-bond formation of the methoxyl oxygen atom, with the hydroxyl group in another molecule.

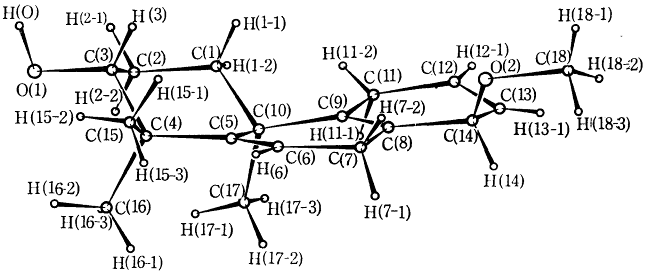


Fig. 1. The molecular configuration of II and the numbering system of the atoms.

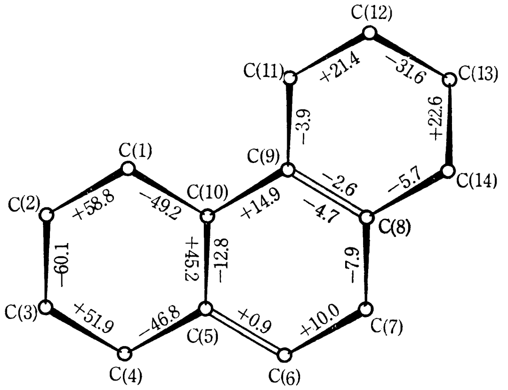


Fig. 2. The torsion angles (°) for the tricyclic system.

Table 4. The bond distances with their standard deviations (Å)
The standard deviations given in parentheses refer to the last decimal position.

(a) The bond distances between the non-hydrogen atoms

C(1)–C(2)	1.525(3)	C(5)–C(6)	1.326(3)	C(10)–C(17)	1.548(4)
C(1)–C(10)	1.551(4)	C(5)–C(10)	1.539(4)	C(11)–C(12)	1.468(6)
C(2)–C(3)	1.518(5)	C(6)–C(7)	1.485(3)	C(12)–C(13)	1.343(10)
C(3)–C(4)	1.539(5)	C(7)–C(8)	1.491(4)	C(13)–C(14)	1.491(8)
C(3)–O(1)	1.422(3)	C(8)–C(9)	1.330(3)	C(14)–O(2)	1.427(4)
C(4)–C(5)	1.548(3)	C(8)–C(14)	1.516(3)	C(18)–O(2)	1.405(3)
C(4)–C(15)	1.541(4)	C(9)–C(10)	1.538(3)		
C(4)–C(16)	1.545(4)	C(9)–C(11)	1.522(5)		

(b) The bond distances involving the hydrogen atoms

C(1)–H(1–1)	0.95(4)	C(11)–H(11–2)	0.86(7)	C(16)–H(16–3)	0.92(7)
C(1)–H(1–2)	0.92(4)	C(12)–H(12–1)	0.92(7)	C(17)–H(17–1)	0.92(4)
C(2)–H(2–1)	1.00(5)	C(13)–H(13–1)	0.73(5)	C(17)–H(17–2)	0.95(7)
C(2)–H(2–2)	0.88(5)	C(14)–H(14)	1.02(5)	C(17)–H(17–3)	0.89(6)
C(3)–H(3)	0.95(3)	C(15)–H(15–1)	1.01(5)	C(18)–H(18–1)	0.98(6)
C(6)–H(6)	1.01(4)	C(15)–H(15–2)	0.92(4)	C(18)–H(18–2)	0.91(7)
C(7)–H(7–1)	0.95(6)	C(15)–H(15–3)	0.94(7)	C(18)–H(18–3)	1.08(11)
C(7)–H(7–2)	0.91(4)	C(16)–H(16–1)	0.98(6)	O(1)–H(O)	0.88(7)
C(11)–H(11–1)	1.01(8)	C(16)–H(16–2)	1.02(5)		

TABLE 5. THE BOND ANGLES WITH THEIR STANDARD DEVIATIONS (°)
The standard deviations given in parentheses refer to the last decimal position.

C(2)-C(1)-C(10)	113.1(2)	C(4)-C(3)-H(3)	107(2)
C(1)-C(2)-C(3)	110.9(2)	O(1)-C(3)-H(3)	110(2)
C(2)-C(3)-C(4)	112.3(3)	C(5)-C(6)-H(6)	117(2)
C(2)-C(3)-O(1)	110.8(2)	C(7)-C(6)-H(6)	117(2)
C(4)-C(3)-O(1)	108.6(2)	C(6)-C(7)-H(7-1)	107(3)
C(3)-C(4)-C(5)	108.9(2)	C(6)-C(7)-H(7-2)	110(2)
C(3)-C(4)-C(15)	107.2(2)	C(8)-C(7)-H(7-1)	111(4)
C(3)-C(4)-C(16)	111.0(2)	C(8)-C(7)-H(7-2)	110(2)
C(5)-C(4)-C(15)	111.6(2)	H(7-1)-C(7)-H(7-2)	105(4)
C(5)-C(4)-C(16)	112.0(2)	C(9)-C(11)-H(11-1)	107(5)
C(15)-C(4)-C(16)	106.0(3)	C(9)-C(11)-H(11-2)	111(4)
C(4)-C(5)-C(6)	120.1(2)	C(12)-C(11)-H(11-1)	111(5)
C(4)-C(5)-C(10)	119.5(2)	C(12)-C(11)-H(11-2)	121(4)
C(6)-C(5)-C(10)	120.4(2)	H(11-1)-C(11)-H(11-2)	90(6)
C(5)-C(6)-C(7)	125.6(3)	C(11)-C(12)-H(12-1)	113(4)
C(6)-C(7)-C(8)	114.0(2)	C(13)-C(12)-H(12-1)	122(4)
C(7)-C(8)-C(9)	122.4(2)	C(12)-C(13)-H(13-1)	129(4)
C(7)-C(8)-C(14)	113.9(2)	C(14)-C(13)-H(13-1)	109(4)
C(9)-C(8)-C(14)	123.6(3)	C(8)-C(14)-H(14)	108(3)
C(8)-C(9)-C(10)	123.1(3)	C(13)-C(14)-H(14)	110(3)
C(8)-C(9)-C(11)	120.5(2)	O(2)-C(14)-H(14)	104(3)
C(10)-C(9)-C(11)	116.2(2)	C(4)-C(15)-H(15-1)	109(3)
C(1)-C(10)-C(5)	108.9(2)	C(4)-C(15)-H(15-2)	109(2)
C(1)-C(10)-C(9)	109.3(2)	C(4)-C(15)-H(15-3)	114(4)
C(1)-C(10)-C(17)	109.9(2)	H(15-1)-C(15)-H(15-2)	110(4)
C(5)-C(10)-C(9)	112.2(2)	H(15-1)-C(15)-H(15-3)	108(5)
C(5)-C(10)-C(17)	110.6(2)	H(15-2)-C(15)-H(15-3)	107(5)
C(9)-C(10)-C(17)	106.0(2)	C(4)-C(16)-H(16-1)	109(3)
C(9)-C(11)-C(12)	114.5(3)	C(4)-C(16)-H(16-2)	105(3)
C(11)-C(12)-C(13)	122.0(7)	C(4)-C(16)-H(16-3)	109(4)
C(12)-C(13)-C(14)	119.8(5)	H(16-1)-C(16)-H(16-2)	111(4)
C(8)-C(14)-C(13)	113.5(3)	H(16-1)-C(16)-H(16-3)	117(5)
C(8)-C(14)-O(2)	107.0(2)	H(16-2)-C(16)-H(16-3)	105(5)
C(13)-C(14)-O(2)	113.6(4)	C(10)-C(17)-H(17-1)	116(3)
C(14)-O(2)-C(18)	115.2(3)	C(10)-C(17)-H(17-2)	114(4)
C(2)-C(1)-H(1-1)	111(2)	C(10)-C(17)-H(17-3)	110(4)
C(2)-C(1)-H(1-2)	109(3)	H(17-1)-C(17)-H(17-2)	103(5)
C(10)-C(1)-H(1-1)	107(2)	H(17-1)-C(17)-H(17-3)	105(4)
C(10)-C(1)-H(1-2)	109(3)	H(17-2)-C(17)-H(17-3)	108(6)
H(1-1)-C(1)-H(1-2)	107(4)	O(2)-C(18)-H(18-1)	107(4)
C(1)-C(2)-H(2-1)	108(3)	O(2)-C(18)-H(18-2)	110(4)
C(1)-C(2)-H(2-2)	110(3)	O(2)-C(18)-H(18-3)	117(6)
C(3)-C(2)-H(2-1)	109(3)	H(18-1)-C(18)-H(18-2)	121(6)
C(3)-C(2)-H(2-2)	109(3)	H(18-1)-C(18)-H(18-3)	96(7)
H(2-1)-C(2)-H(2-2)	110(4)	H(18-2)-C(18)-H(18-3)	105(7)
C(2)-C(3)-H(3)	107(2)	C(3)-O(1)-H(O)	106(5)

The bond lengths and angles calculated with the final coordinates are listed in Tables 4 and 5 respectively. In the present molecule also, the C(12)–C(13) distance is found to be unusually shorter than the normal C–C single bond length. A detailed account of this remarkable shortening will be given later. The intramolecular hydrogen-hydrogen distances less than 2.40 Å are listed in Table 6.

The conformation of the A ring in II is closely parallel to that in III; for example, the greatest of the differences between the corresponding torsion angles is only 2.6°, and the average torsion angles for the two

TABLE 6. THE INTRAMOLECULAR H···H CONTACTS (Å)
The standard deviations are given in parentheses.

H(1-1)···H(2-1)	2.35(4)	H(3) ···H(O)	2.06(5)	H(11-2)···H(12-1)	2.34(7)
H(1-2)···H(2-1)	2.33(5)	H(6) ···H(7-2)	2.36(5)	H(12-1)···H(13-1)	2.30(9)
···H(2-2)	2.29(6)	···H(15-1)	2.25(6)	H(13-1)···H(14)	2.21(9)
···H(11-2)	2.10(6)	···H(15-3)	2.09(5)	H(15-2)···H(16-2)	2.33(7)
H(2-1)···H(3)	2.32(5)	H(11-1)···H(12-1)	2.37(10)	H(16-3)···H(17-1)	2.19(8)
H(2-2)···H(16-3)	2.24(11)	···H(17-3)	2.12(10)		

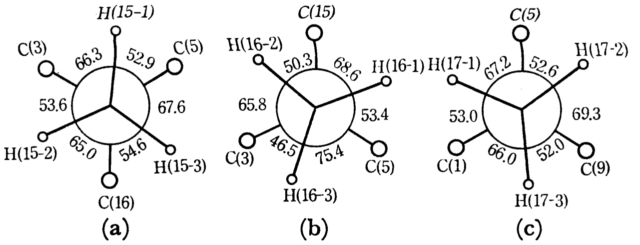


Fig. 3. The Newman projections along the bonds, (a) C(4)–C(15), (b) C(4)–C(16), and (c) C(10)–C(17).

rings are also in good agreement with each other. The distribution of the valence angles in the A ring is similar to those in III and in the acetolysis product of II, hereafter called IV;[4] *i.e.*, the valence angles at the C(1) and C(3) atoms are significantly greater than the normal tetrahedral angle. This may be due to the existence of the exocyclic double bond, C(5)=C(6). The conformations of the three methyl groups attached to the A ring are shown in Fig. 3. The deviations of the two axial methyl groups, $C(16)H_3$ and $C(17)H_3$, from the staggered conformation, 10° and 7°, are both slightly smaller than the corresponding values for III. On the other hand, the conformation of the equatorial methyl group, $C(15)H_3$, deviates by about 6° from the staggered arrangement; this value is about 3° larger than that for III. These small variances of the rotation angles found in II and III probably result from the delicate difference in the conformations of the tricyclic systems. The hydroxyl group, O(1)H, is equatorially bonded to the A ring. The azimuthal angle of the O(1)–H(O) and C(3)–H(3) bonds around the C(3)–O(1) bond is about 33°. This approach to the eclipsed arrangement may be attributable to the formation of the O(1)–H(O)···O(2′) hydrogen bond. In fact, the O(1)–H(O)–O(2′) angle is about 180°.

Table 7. The deviations (Å) of the atoms from the least-squares plane

C(7)	0.030	C(11)	0.027
C(8)	0.019	C(12)[a]	0.105
C(9)	0.029	C(13)[a]	−0.246
C(10)	−0.053	C(14)	−0.052

a) These atoms were omitted from the calculation of the least-squares plane.

With respect to the plane which bisects the C(5)–C(10)–C(9) or C(6)–C(7)–C(8) angle, the conformation of the B ring in II is less symmetrical than that in IV. Although one of the two ethylenic parts, >C(5)=C(6)<, holds a good planarity, the other, >C(8)=C(9)<, deviates to some extent from a planar configuration. The deviations of the atoms from the least-squares plane through the C(7), C(8), C(9), C(10), C(11), and C(14) atoms are given in Table 7. The angle between this plane and the least-squares plane through the C(4), C(5), C(6), C(7), and C(10) atoms is about 11.8°; this is about 3.3° and 8.2° smaller than the corresponding angles for III and IV respectively.

As will be seen in Fig. 1, the C ring in II is unusually flattened, although it keeps approximately the C_2 symmetry characteristic of the half-chair conformation. The C(12) and C(13) atoms are, respectively, only about 0.14 and 0.18 Å displaced above and below the mean plane through the other four atoms in the ring; the sum of these deviations, 0.32 Å, is remarkably smaller than that in IV, 0.73 Å, and that in cyclohexene, 0.7346 Å.[5] It is of great interest to examine why the C ring in II is forced to take such an unusually-flattened conformation. The closest approach of the methylene groups, $C(1)H_2$ and $C(11)H_2$, is found between the two equatorial hydrogen atoms, H(1–2) and H(11–2), their distance being about 2.10 Å; this is only slightly greater than the distance between the overcrowded hydrogen atoms in phenanthrene, 2.04 Å.[6] Since the less the equatorial nature of the H(11–2) atom is, the more distant the H(1–2) and H(11–2) atoms become, it is clear that the flattened conformation of the C ring prevents the two hydrogen atoms from approaching each other at an extremely small distance. The unusual conformation of the C ring is, therefore, perhaps caused mainly by the strong steric repulsion between the H(1–2) and H(11–2) atoms. On the other hand, an X-ray study of IV has revealed that the C ring in IV takes the normal half-chair form in which the axial positions in II become equatorial and *vice versa*.[4] This is probably because the equatorial hydrogen atoms, H(1–2) and H(11–1), maintain a distance of about 2.23 Å without any large deformation of the C ring. If this is the reason, then the question arises of why the C ring in II does not take the same conformation as that in IV. The most conceivable reason is that the allylic axial methoxyl group might have the effect of stabilizing the cyclohexene system, probably by allowing the transfer of some π-electrons on the C(8)=C(9) double bond into the overlapping antibonding orbital of the C(14)–O(2) bond.[7] The stabilization due to the delocalization of π-electrons would overcome the energy loss resulting from the great deformation of the C ring.

The length of the C(12)–C(13) bond is found to be about 1.343 Å; this is almost equal to the value for III, 1.340 Å. However, both the results of elemental analysis and the NMR spectrum clearly show that the C(12)–C(13) bond should be a single one.[1] This conflict may be resolved by taking account of the unusual thermal vibrations of the C(12) and C(13) atoms. The thermal ellipsoids of atoms in the C ring are shown in Fig. 4, while the root-mean-square deviations and direction cosines in the principal axes of the ellipsoids are given in Table 8. It is found that all

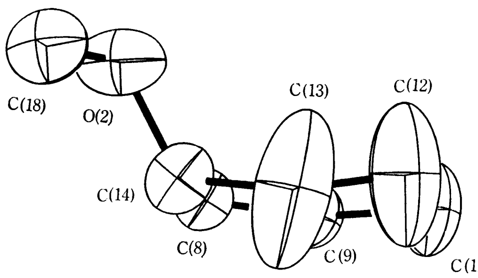


Fig. 4. The thermal behavior of the C ring. The thermal ellipsoids are scaled to enclose 50% probability.

TABLE 8. THE ROOT-MEAN-SQUARE DEVIATIONS AND DIRECTION COSINES IN THE PRINCIPAL AXES OF THE THERMAL ELLIPSOIDS

$B_i = 8\pi^2 u_i^2$ where u_i is the root-mean-square deviation corresponding to the ith axis of the ellipsoid.

C_{ia}, C_{ib}, and C_{ic} are the direction cosines of the i axis with respect to the orthogonal coordinate axes by **b** × **c***, **b**, and **c***.

Atom	Axis i	B_i (Å^2)	u_i (Å)	C_{ia}	C_{ib}	C_{ic}
C (8)	1	2.75	0.187	−0.827	−0.549	−0.120
	2	3.31	0.205	−0.069	−0.113	0.991
	3	4.03	0.226	−0.558	0.828	0.056
C (9)	1	2.45	0.176	−0.412	−0.471	−0.780
	2	3.55	0.212	0.661	0.435	−0.611
	3	4.13	0.229	−0.627	0.768	−0.132
C (11)	1	2.67	0.184	−0.398	−0.674	−0.623
	2	4.52	0.239	−0.686	−0.233	0.690
	3	9.07	0.339	−0.610	0.702	−0.369
C (12)	1	2.55	0.180	−0.534	−0.718	−0.446
	2	5.89	0.273	−0.662	0.027	0.749
	3	21.36	0.520	−0.526	0.695	−0.489
C (13)	1	2.57	0.180	−0.718	−0.677	−0.160
	2	5.82	0.271	−0.310	0.105	0.945
	3	27.76	0.593	−0.624	0.728	−0.285
C (14)	1	2.92	0.192	−0.860	−0.499	0.102
	2	4.16	0.229	0.171	−0.092	0.981
	3	5.59	0.266	0.480	−0.862	−0.165
O (2)	1	2.72	0.186	−0.848	−0.389	0.359
	2	4.32	0.234	0.527	−0.681	0.508
	3	9.16	0.341	−0.047	−0.620	−0.783
C (18)	1	3.18	0.201	−0.747	−0.467	0.473
	2	5.68	0.268	0.664	−0.548	0.508
	3	7.35	0.305	−0.022	−0.694	−0.720

the six atoms in the C ring vibrate most vigorously in a direction almost perpendicular to the mean plane of the ring. Above all, the anisotropy of the thermal motions of the C(12) and C(13) atoms is very conspicuous; their greatest root-mean-square deviations are about 0.52 and 0.59 Å respectively. In a previous paper,[2] we pointed out that, even though the C(12)–C(13) bond distance is corrected for these large thermal motions, the correction is very small so long as the riding motion is assumed, but that if a highly-correlated antiparallel motion is assumed for the two atoms, the corrected distance becomes too large (1.73 Å). This suggests that the thermal motions of the C(12) and C(13) atoms may contain both parallel and antiparallel components.

Let us consider a one-dimensional harmonic oscillator which moves along the x axis, with the point 0′ as the equilibrium position. If the 0′ point further vibrates harmonically round the origin of the coordinates, 0, much more slowly than the oscillator moves round the 0′ point, then the probability of finding simultaneously the 0′ point between X and $X+\mathrm{d}X$ and the oscillator between x and $x+\mathrm{d}x$, $P(x, X)\mathrm{d}x\mathrm{d}X$, may be represented approximately by the following equation:

$$P(x, X)\mathrm{d}x\mathrm{d}X \propto \exp\left\{-\frac{X^2}{2\bar{u}_1{}^2}\right\} \times \exp\left\{-\frac{(x-X)^2}{2\bar{u}_2{}^2}\right\}\mathrm{d}x\mathrm{d}X$$
$$= \exp\left\{-\frac{1}{2}\left(\frac{1}{\bar{u}_1{}^2}+\frac{1}{\bar{u}_2{}^2}\right)\left(X-\frac{x}{1+\bar{u}_2{}^2/\bar{u}_1{}^2}\right)^2\right\}$$
$$\times \exp\left\{-\frac{x^2}{2(\bar{u}_1{}^2+\bar{u}_2{}^2)}\right\}\mathrm{d}x\mathrm{d}X,$$

where $\bar{u}_1$ and $\bar{u}_2$ are, respectively, the root-mean-square amplitude of the 0′ point and that of the oscillator with respect to the vibrating point, 0′. Accordingly, the probability of finding the oscillator between x and $x+\mathrm{d}x$, $P(x)\mathrm{d}x$, is given by the equation:

$$P(x)\mathrm{d}x = \int_{-\infty}^{\infty} P(x, X)\mathrm{d}x\mathrm{d}X \propto \exp\left\{-\frac{x^2}{2(\bar{u}_1{}^2+\bar{u}_2{}^2)}\right\}\mathrm{d}x$$
$$= \exp\left\{-\frac{x^2}{2\bar{u}^2}\right\}\mathrm{d}x.$$

The apparent mean-square amplitude of the oscillator, $\bar{u}^2$, is thus given by the sum of $\bar{u}_1{}^2$ and $\bar{u}_2{}^2$. The thermal motions of the C(12) and C(13) atoms in the direction perpendicular to the mean plane of the C ring might be approximated by such a special harmonic oscillator model. In this case, the oscillation of the 0′ point corresponds to the parallel vibrational components of the two atoms arising from the thermal motion of the whole molecule as a rigid body, while the harmonic motion of the oscillator with respect to the 0′ point corresponds to the antiparallel components resulting from the internal vibration of the C ring. Since the thermal vibration of the C(11) atom does not seem to be very closely related to the antiparallel motions of the C(12) and C(13) atoms, it would be reasonable to use its greatest root-mean-square deviation as the approximate $\bar{u}_1$ value of the two atoms. From this value of $\bar{u}_1$, 0.34 Å, and the observed values of $\bar{u}$ for the C(12) and C(13) atoms, 0.52 and 0.59 Å, we obtain $\bar{u}_2 = 0.39$ and 0.48 Å for these two atoms respectively. In case of the antiparallel motions, the mean-square distance, $\bar{r}^2$, is given by the equation: $\bar{r}^2 = s^2 + r_0{}^2$, where s is the sum of the $\bar{u}_2$ values of the two atoms and where r_0 is the observed distance between their equilibrium positions. Since both the effect on the $\bar{r}^2$ of the parallel motions of the C(12) and C(13) atoms and that of their thermal vibrations in the directions parallel with the mean plane of the C ring seem to be very small, it is expected that the C(12)–C(13) distance can be corrected to a considerable extent by using this equation. In fact, the value thus obtained, 1.60 Å, is much closer to the standard C–C distance, 1.54 Å, than the uncorrected value, 1.34 Å. That the correction is too great is probably in part due to the underestimation of the $\bar{u}_1$ value used in the calculation, and in part to the presence of the anharmonic components in the thermal motions of the C(12) and C(13) atoms.

The complicated thermal motions found in II are probably caused by the highly-strained conformation of the C ring. Compared with the ordinary half-chair form, such an unusually-flattened conformation is considerably unstable. This would bring about the vigorous, antiparallel vibrations of the C(12) and C(13) atoms. That, in the cyclohexene ring, the bond corresponding to the C(12)–C(13) is too short has previously

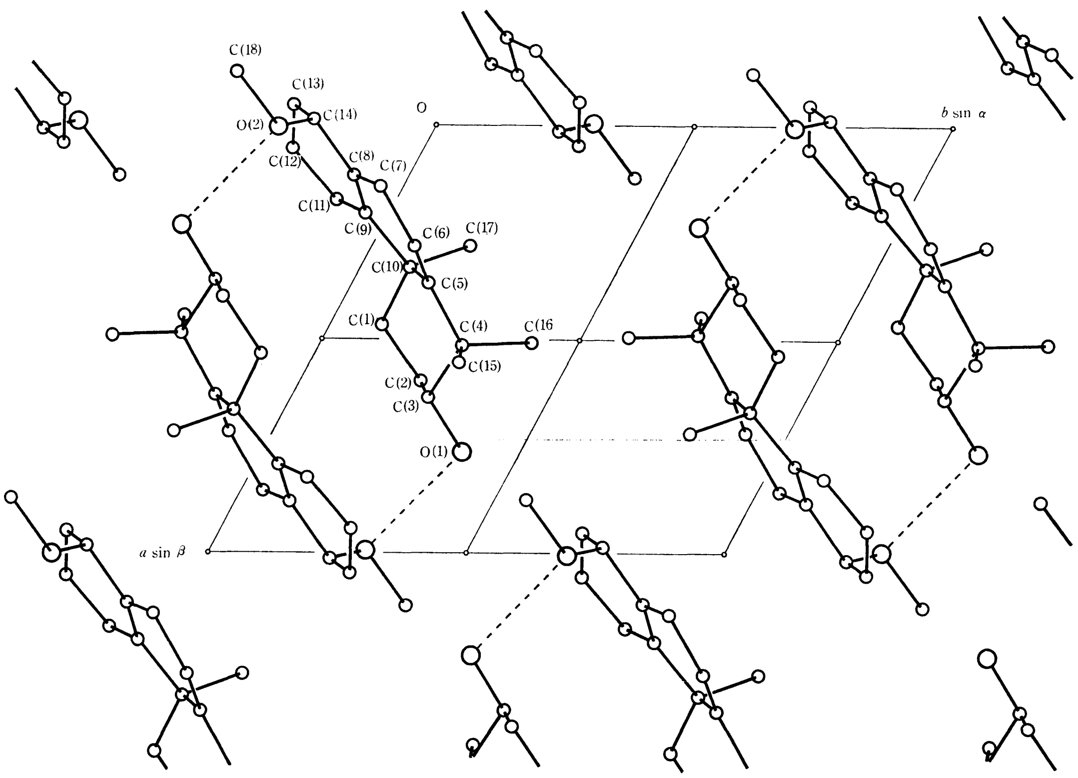


Fig. 5. The molecular arrangement viewed along the c axis.

been noticed in canthaxanthin[8] and in the *trans* isomer of β-ionylidenecrotonic acid.[9] In the former case, the shortening was interpreted as being due to the existence of two separate ring conformations in one single crystal, while, in the latter case, it was not clear whether the shortening was attributable to the conformational disorder or to the large asymmetric vibrations of the ring. When the C ring in II flips from one normal half-chair form to the other, the O(2) atom is shifted by about 0.7 Å. This shows that, if the present crystal had a disordered structure with respect to the two possible half-chair conformations of the C ring, it would contain two kinds of O(2)···O(1′) hydrogen bonding; for the normal half-chair form (A-form) where the O(2) atom is axial, the O(2)···O(1′) distance is estimated to be about 2.7 Å, while, for the other (B-form) where the O(2) atom is equatorial, it is about 3.2 Å.* In the case of such a disordered structure, the number of molecules with the A-form would be considerably larger in the crystal of II than in the crystal of III; in other words, the apparent conformation of the C ring in II would be much closer to the A-form than that in III, because, although the O(2) atom does not take part in the hydrogen-bond formation in the latter crystal, it can form a stable hydrogen bond in the former crystal if the C ring takes the A-form. However, in fact, almost the same conformations are observed for II and III. Accordingly, in the present case, it seems more reasonable to consider the remarkable shortening of the C(12)–C(13) bond as due to the special thermal vibrations of the C(12) and C(13) atoms rather than to the conformational disorder.

As has already been mentioned, out of the twenty-eight hydrogen atoms in a molecule, two were not located in the difference Fourier map. These two are the same axial hydrogen atoms at the C(12) and C(13) atoms that could not be found in the crystal structure of III. The fact that the axial hydrogen atoms are difficult to locate is obviously related to the complicated thermal vibrations of the C(12) and C(13) atoms.

The O(2)–C(18) bond makes an azimuthal angle of about 41° with the C(14)–H(14) bond and one of about 78.8° with the C(13)–C(14) bond around the C(14)–O(2) bond.

The molecular arrangement viewed along the c axis

Table 9. The principal intermolecular distances (Å)
The standard deviations are given in parentheses.

(1) I···II (III···I)	
C(7)···C(11)	3.878(4)
C(15)···C(2)	3.882(5)
(2) I···IV (V···I)	
O(1)···C(12)	3.849(6)
···C(13)	3.586(7)
(3) I···VI (VII···I)	
O(1)···C(18)	3.476(4)
C(2)···C(18)	3.726(3)
(4) I···VIII (VIII···I)	
C(7)···C(7)	3.841(6)
···C(8)	3.803(5)
···C(14)	3.960(5)
(5) I···IX (IX···I)	
O(1)···O(2)	2.803(4)
···C(14)	3.784(4)
···C(18)	3.607(5)
O(2)···C(3)	3.525(4)
C(3)···C(8)	3.865(4)

I: x/a, y/b, z/c (given in Table 3). II: $x/a, y/b, 1+z/c$. III: $x/a, y/b, -1+z/c$. IV: $1+x/a, 1+y/b, z/c$. V: $-1+x/a, -1+y/b, z/c$. VI: $1+x/a, 1+y/b, -1+z/c$. VII: $-1+x/a, -1+y/b, 1+z/c$. VIII: $-x/a, -y/b, 1-z/c$. IX: $1-x/a, -y/b, 1-z/c$.

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* In this estimation, it was assumed that the C(13) atom deviates by 0.367 Å from the plane of the C(8)=C(9) double bond, and that the bond distances and angles for the C(8) and C(14) atoms are equal to those in Tables 4 and 5.

is shown in Fig. 5, while the short intermolecular distances are listed in Table 9. The molecules make a hydrogen bond, O(1)–H···O(2′), with each other at a distance of about 2.80 Å to form a dimer around a center of symmetry. The hydrogen-bonded dimers thus formed are further held together mainly by the ordinary van der Waals interactions.

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