The Crystal Structure of *d,l*-1,1,4a*α*-Trimethyl-2*α*-hydroxy-8*α*-acetoxy-1,2,3,4,4a,5,6,7,8,9-decahydrophenanthrene

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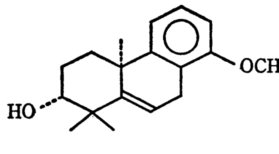
The conformation of *d,l*-1,1,4aα-trimethyl-2α-hydroxy-8α-acetoxy-1,2,3,4,4a,5,6,7,8,9-decahydrophenanthrene has been studied by means of X-ray methods. The crystals are triclinic, with two molecules in a unit cell with the dimensions of $a=11.463$, $b=11.509$, $c=7.430$ Å, $\alpha=84°42'$, $\beta=102°47'$, and $\gamma=115°40'$. The space group is P$\bar{1}$. The intensity data were collected on an automatic four-circle diffractometer with Cu*Kα* radiation. The structure was solved by the symbolic-addition method, and was refined by the block-diagonal-matrix least-squares method with anisotropic temperature factors for all the non-hydrogen atoms. From a difference Fourier map, all the 28 hydrogen atoms were also found. Further least-squares refinement including these hydrogen atoms reduced the *R* factor to 5.4%. In the present molecule, the cyclohexene ring has the normal half-chair conformation, and does not show the unusual behavior found in the *p*-bromobenzoate of 1,1,4aα-trimethyl-2α-hydroxy-8β-methoxy-1,2,3,4,4a,5,6,7,8,9-decahydrophenanthrene. The 8α-acetoxyl group, like the 8β-methoxyl group in the *p*-bromobenzoate, takes the axial orientation notwithstanding the inversion of the configuration. Such a conformation seems to be the preferred one for a cyclohexene ring which has a methoxyl or an acetoxyl group at the allylic position.

It has recently been found that the Birch reduction of 1,1,4aα-trimethyl-2α-hydroxy-8-acetoxy-1,2,3,4,4a,9-hexahydrophenanthrene, I, affords an unusual product, II, and that, in the acetolysis of II, the methoxyl group is much more easily replaced with an acetoxyl group than those in usual allyl methyl ethers.[1] On the other hand, for the purpose of inquiring into the cause of the high reactivity, the stereostructure of II has been studied by means of the X-ray crystallographic analysis of its *p*-bromobenzoate derivative, III.[2] The study has revealed not only that the methoxyl group is axially bonded to the cyclohexene ring with a considerably flattened half-chair form, but also that the two carbon atoms in the ring vibrate vigorously in a direction almost perpendicular to the mean plane of the ring. In order to examine whether or not these remarkable features are also observed in the acetolysis product, IV, and to establish the configuration of the acetoxyl group, an X-ray analysis of IV has now been carried out.



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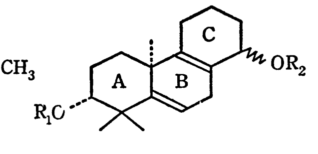

II $R_1=H$, $R_2=CH_3$
III $R_1=BrC_6H_4CO$, $R_2=CH_3$
IV $R_1=H$, $R_2=CH_3CO$

Experimental

Colorless, single crystals of IV (racemate), $C_{19}H_{28}O_3$, mp 146—7°C, were grown in an ether solution. A sample with dimensions of about 0.1×0.2×0.4 mm was cut out of one of the single crystals and 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*Kα* radiation ($\lambda=1.54178$ Å). The space group was assumed to be P$\bar{1}$ at the beginning of the study; this choice was confirmed later by successful refinement. The intensities of reflections with 2θ values up to 140° were collected on an automatic four-circle diffractometer at this University, using Cu*Kα* radiation monochromatized with a LiF crystal. The intensity measurement was made by the use of the ω-2θ scanning technique. The scan rate was about 0.5°(ω)/min, and the background was measured for each reflection for 30—60 s at the beginning and end of each scanning range. The intensity data were corrected for the usual Lorentz and polarization factors, but not for the absorption effect. Out of the structure factors thus obtained, 2769 above $2\sigma(F)$ were selected for the structural study.

Table 1. The crystal data

Crystal system Space group	Triclinic P$\bar{1}$
a	11.463±0.003 Å
b	11.509±0.003
c	7.430±0.003
α	84°42′±3′
β	102°47′±3′
γ	115°40′±3′
Z	2
D_x	1.173 g/cm^3

Structure Determination

The structure was elucidated by means of the symbolic addition method[3] on the basis of 585 $|E|$ values above 1.30. After 286 phases had been expressed by three symbols, A, B, and C, the values of the R factor ($R=\sum|E_o-E_c|/\sum|E_o|$) were calculated for all eight possible combinations of the numerical values of the symbols. Since it was certain that the set ($A=B=C=0$) with the lowest R value, 0.171, did not lead to the true structure, an E-Fourier synthesis was carried

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[1] N. Hamanaka, T. Okuno, T. Nakajima, A. Furusaki, and T. Matsumoto, *Chem. Lett.*, **1972**, 1037.

[2] A. Furusaki, N. Hamanaka, and T. Matsumoto, This Bulletin, **46**, 434 (1973).

[3] J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).

TABLE 2. 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)	3613(2)	3557(2)	2033(2)	C(9)	8460(2)	3017(2)	3046(2)
O(2)	10612(1)	2007(1)	5789(2)	C(10)	6967(2)	2618(2)	2483(2)
O(3)	12079(3)	2850(3)	8346(3)	C(11)	9247(2)	3517(3)	1533(3)
C(1)	6709(2)	3594(2)	1058(2)	C(12)	10544(2)	3386(3)	1981(4)
C(2)	5281(2)	3413(2)	640(2)	C(13)	11289(2)	3936(2)	3873(4)
C(3)	4895(2)	3569(2)	2376(3)	C(14)	10496(2)	3234(2)	5326(3)
C(4)	4981(2)	2554(2)	3863(2)	C(15)	4770(2)	2958(3)	5637(3)
C(5)	6346(1)	2531(2)	4144(2)	C(16)	3870(2)	1212(2)	3303(4)
C(6)	6964(2)	2383(2)	5829(2)	C(17)	6361(2)	1273(2)	1556(3)
C(7)	8281(2)	2355(2)	6272(3)	C(18)	11403(2)	1940(3)	7335(3)
C(8)	9040(2)	2872(2)	4757(2)	C(19)	11409(4)	652(4)	7594(6)

(2) The anisotropic temperature factors

These are expressed as

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

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{31}
O(1)	114(2)	227(3)	234(3)	223(4)	−14(4)	23(4)
O(2)	107(1)	100(1)	264(3)	116(2)	−65(3)	−73(3)
O(3)	206(3)	217(3)	329(5)	266(5)	−178(6)	−234(6)
C(1)	96(2)	106(2)	140(3)	107(3)	33(3)	56(3)
C(2)	102(2)	133(2)	151(3)	136(3)	24(4)	14(4)
C(3)	86(2)	120(2)	180(3)	117(3)	−10(4)	22(3)
C(4)	77(2)	113(2)	171(3)	81(3)	5(4)	52(3)
C(5)	74(1)	75(1)	142(3)	60(2)	4(3)	41(3)
C(6)	94(2)	115(2)	140(3)	90(3)	22(3)	57(3)
C(7)	104(2)	139(2)	152(3)	123(3)	38(4)	10(4)
C(8)	77(1)	79(1)	179(3)	70(2)	−28(3)	18(3)
C(9)	77(1)	81(1)	167(3)	72(2)	2(3)	51(3)
C(10)	77(1)	78(1)	130(3)	71(2)	−11(3)	27(3)
C(11)	106(2)	163(3)	226(4)	145(4)	91(5)	133(5)
C(12)	118(2)	163(3)	338(6)	162(4)	111(7)	197(6)
C(13)	77(2)	119(2)	422(7)	84(3)	45(6)	82(5)
C(14)	82(2)	89(2)	265(4)	84(3)	−63(4)	−31(4)
C(15)	122(2)	204(3)	202(4)	189(5)	26(6)	117(5)
C(16)	79(2)	129(2)	335(6)	37(3)	12(6)	65(5)
C(17)	112(2)	97(2)	210(4)	90(3)	−81(4)	12(4)
C(18)	103(2)	151(3)	254(5)	154(4)	−25(5)	−30(5)
C(19)	197(4)	177(4)	436(9)	234(7)	75(9)	−62(10)

(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	Atom	x/a	y/b	z/c	B
H(1-1)	729(2)	449(2)	157(3)	23(4)	H(14)	1085(3)	377(2)	639(4)	29(5)
H(1-2)	695(2)	353(2)	−4(4)	26(4)	H(15-1)	559(4)	384(3)	622(5)	51(7)
H(2-1)	519(2)	405(2)	−23(3)	23(4)	H(15-2)	400(3)	307(3)	535(4)	39(6)
H(2-2)	469(3)	255(2)	10(4)	27(4)	H(15-3)	468(4)	227(4)	656(5)	54(7)
H(3)	556(2)	447(2)	298(3)	24(4)	H(16-1)	395(4)	56(4)	421(6)	57(8)
H(6)	657(3)	226(2)	686(4)	28(5)	H(16-2)	308(4)	122(4)	326(5)	53(7)
H(7-1)	822(3)	150(3)	655(4)	32(5)	H(16-3)	384(3)	91(3)	210(5)	45(6)
H(7-2)	880(4)	285(4)	740(5)	51(7)	H(17-1)	539(3)	100(3)	97(4)	39(6)
H(11-1)	869(3)	306(3)	37(5)	45(7)	H(17-2)	644(3)	66(3)	250(4)	36(5)
H(11-2)	943(3)	449(3)	127(4)	42(6)	H(17-3)	688(3)	130(3)	64(4)	39(6)
H(12-1)	1109(4)	389(3)	100(5)	53(7)	H(19-1)	1120(7)	30(7)	873(10)	108(16)
H(12-2)	1036(3)	244(3)	195(4)	42(6)	H(19-2)	1059(6)	−2(6)	704(8)	90(13)
H(13-1)	1212(3)	394(3)	419(4)	42(6)	H(19-3)	1207(7)	58(7)	779(10)	112(16)
H(13-2)	1143(3)	489(3)	391(4)	41(6)	H(O)	327(4)	328(4)	96(6)	61(8)

out using 558 phases based on the set ($A=B=0$, $C=\pi$) with the second lowest R, 0.199. As was expected, the resulting E-map yielded the locations of all the non-hydrogen atoms. The structure thus obtained was refined by the block-diagonal-matrix least-squares method, first with individual isotropic temperature factors and then with anisotropic thermal parameters for all the atoms. In this way, the value of the discrepancy factor, $R(R=\sum|F_o-F_c|/\sum|F_o|)$, dropped to 11.2%. After the 28 hydrogen atoms were located in a difference Fourier map, the least-squares refinement was further repeated including these hydrogen atoms with isotropic temperature factors. In this refinement, the following weighting scheme was used:

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

where $X=|F_o|$, $Y=\sin\theta/\lambda$. The $\sigma(F_o)$ values were calculated from the counting statistics. 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 $<W\Delta|F|^2>$ for all the groups as possible. The final R factor was 5.4%. The atomic parameters thus obtained are listed in Table 2.

The calculations in the present study were carried out on a FACOM 230—60 computer at the Computer Center of Hokkaido University using our own programs. The atomic scattering factors were taken from the International Tables for X-ray Crystallography (1962), Vol. III.

Tables of the observed and calculated structure factors are preserved by the Chemical Society of Japan. (Document No. 7309).

Results and Discussion

The molecular framework of IV thus obtained is shown in Fig. 1. First of all, it is found that the acetoxyl group has the *cis* relation with the angular methyl,

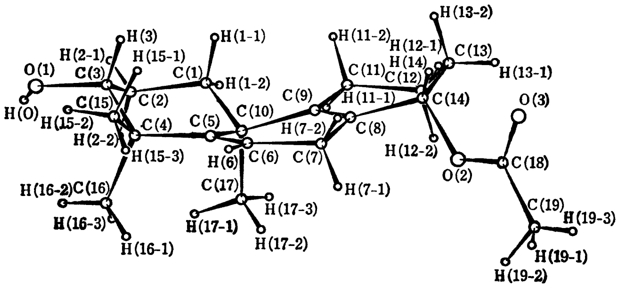

Fig. 1. The molecular framework of IV and the numbering system of the atoms.

TABLE 3. THE BOND DISTANCES WITH THEIR STANDARD DEVIATIONS (Å)

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

Bond	D	σ	Bond	D	σ
C(1)-C(2)	1.520	0.003	C(8)-C(9)	1.329	0.002
C(1)-C(10)	1.549	0.003	C(8)-C(14)	1.503	0.003
C(2)-C(3)	1.502	0.003	C(9)-C(10)	1.534	0.002
C(3)-C(4)	1.552	0.003	C(9)-C(11)	1.513	0.003
C(3)-O(1)	1.429	0.003	C(10)-C(17)	1.552	0.003
C(4)-C(5)	1.544	0.003	C(11)-C(12)	1.520	0.004
C(4)-C(15)	1.537	0.004	C(12)-C(13)	1.507	0.004
C(4)-C(16)	1.537	0.003	C(13)-C(14)	1.510	0.004
C(5)-C(6)	1.330	0.002	C(14)-O(2)	1.477	0.003
C(5)-C(10)	1.531	0.002	C(18)-C(19)	1.480	0.005
C(6)-C(7)	1.487	0.003	C(18)-O(2)	1.316	0.003
C(7)-C(8)	1.496	0.003	C(18)-O(3)	1.203	0.003

(b) The bond distances involving the hydrogen atoms

Bond	D	σ	Bond	D	σ
C(1)-H(1-1)	1.01	0.02	C(14)-H(14)	0.94	0.03
C(1)-H(1-2)	0.93	0.03	C(15)-H(15-1)	1.08	0.03
C(2)-H(2-1)	0.95	0.03	C(15)-H(15-2)	0.93	0.04
C(2)-H(2-2)	0.99	0.02	C(15)-H(15-3)	0.98	0.04
C(3)-H(3)	1.05	0.02	C(16)-H(16-1)	0.98	0.04
C(6)-H(6)	0.94	0.03	C(16)-H(16-2)	0.90	0.05
C(7)-H(7-1)	0.96	0.03	O(16)-H(16-3)	0.97	0.04
C(7)-H(7-2)	0.98	0.03	C(17)-H(17-1)	1.02	0.03
C(11)-H(11-1)	0.99	0.03	C(17)-H(17-2)	0.97	0.03
C(11)-H(11-2)	1.06	0.04	C(17)-H(17-3)	0.99	0.04
C(12)-H(12-1)	1.04	0.04	C(19)-H(19-1)	0.94	0.08
C(12)-H(12-2)	1.02	0.04	C(19)-H(19-2)	0.95	0.05
C(13)-H(13-1)	0.93	0.04	C(19)-H(19-3)	0.77	0.09
C(13)-H(13-2)	1.04	0.04	O(1)-H(O)	0.84	0.04

Table 4. The bond angles with their standard deviations (°)

	Angle	σ		Angle	σ
C(2)-C(1)-C(10)	113.4	0.2	C(5)-C(6)-H(6)	121	2
C(1)-C(2)-C(3)	110.0	0.2	C(7)-C(6)-H(6)	114	2
C(2)-C(3)-C(4)	112.7	0.2	C(6)-C(7)-H(7-1)	112	2
C(2)-C(3)-O(1)	112.4	0.2	C(6)-C(7)-H(7-2)	109	2
C(4)-C(3)-O(1)	110.1	0.2	C(8)-C(7)-H(7-1)	108	2
C(3)-C(4)-C(5)	109.4	0.2	C(8)-C(7)-H(7-2)	109	2
C(3)-C(4)-C(15)	106.6	0.2	H(7-1)-C(7)-H(7-2)	105	3
C(3)-C(4)-C(16)	110.8	0.1	C(9)-C(11)-H(11-1)	109	2
C(5)-C(4)-C(15)	111.6	0.2	C(9)-C(11)-H(11-2)	110	2
C(5)-C(4)-C(16)	110.6	0.2	C(12)-C(11)-H(11-1)	111	2
C(15)-C(4)-C(16)	107.7	0.2	C(12)-C(11)-H(11-2)	110	2
C(4)-C(5)-C(6)	119.9	0.2	H(11-1)-C(11)-H(11-2)	105	3
C(4)-C(5)-C(10)	120.3	0.1	C(11)-C(12)-H(12-1)	108	2
C(6)-C(5)-C(10)	119.7	0.2	C(11)-C(12)-H(12-2)	110	2
C(5)-C(6)-C(7)	124.8	0.2	C(13)-C(12)-H(12-1)	110	2
C(6)-C(7)-C(8)	113.4	0.2	C(13)-C(12)-H(12-2)	110	2
C(7)-C(8)-C(9)	121.9	0.2	H(12-1)-C(12)-H(12-2)	110	3
C(7)-C(8)-C(14)	115.0	0.2	C(12)-C(13)-H(13-1)	113	2
C(9)-C(8)-C(14)	123.0	0.2	C(12)-C(13)-H(13-2)	109	2
C(8)-C(9)-C(10)	122.3	0.2	C(14)-C(13)-H(13-1)	110	2
C(8)-C(9)-C(11)	120.8	0.2	C(14)-C(13)-H(13-2)	106	2
C(10)-C(9)-C(11)	116.8	0.2	H(13-11)-C(13)-H(13-2)	107	3
C(1)-C(10)-C(5)	110.3	0·2	C(8)-C(14)-H(14)	110	2
C(1)-C(10)-C(9)	109.2	0.1	C(13)-(14)-H(14)	108	2
C(1)-C(10)-C(17)	109.3	0.1	O(2)-C(14)-H(14)	109	2
C(5)-C(10)-C(9)	112.1	0.1	C(4)-C(15)-H(15-1)	112	2
C(5)-C(10)-C(17)	109.6	0.1	C(4)-C(15)-H(15-2)	108	2
C(9)-C(10)-C(17)	106.2	0.1	C(4)-C(15)-H(15-3)	110	2
C(9)-C(11)-C(12)	113.1	0.2	H(15-1)-C(15)-H(15-2)	110	3
C(11)-C(12)-C(13)	109.5	0.3	H(15-1)-C(15)-H(15-3)	108	3
C(12)-C(13)-C(14)	111.0	0.2	H(15-2)-C(15)-H(15-3)	109	3
C(8)-C(14)-C(13)	114.8	0.2	C(4)-C(16)-H(16-1)	111	2
C(8)-C(14)-O(2)	105.5	0.2	C(4)-C(16)-H(16-2)	110	3
C(13)-C(14)-O(2)	109.7	0.2	C(4)-C(16)-H(16-3)	115	2
O(2)-C(18)-O(3)	122.8	0.3	H(16-1)-C(16)-H(16-2)	107	4
O(2)-C(18)-C(19)	111.9	0.3	H(16-1)-C(16)-H(16-3)	107	3
O(3)-C(18)-C(19)	125.2	0.3	H(16-2)-C(16)-H(16-3)	107	4
C(14)-O(2)-C(18)	118.5	0.2	C(10)-C(17)-H(17-1)	111	2
C(2)-C(1)-H(1-1)	109	1	C(10)-C(17)-H(17-2)	108	2
C(2)-C(1)-H(1-2)	109	2	C(10)-C(17)-H(17-3)	109	2
C(10)-C(1)-H(1-1)	108	1	H(17-1)-C(17)-H(17-2)	109	3
C(10)-C(1)-H(1-2)	110	2	H(17-1)-C(17)-H(17-3)	112	3
H(1-1)-C(1)-H(1-2)	108	2	H(17-2)-C(17)-H(17-3)	108	3
C(1)-C(2)-H(2-1)	109	2	C(18)-C(19)-H(19-1)	111	5
C(1)-C(2)-H(2-2)	110	1	C(18)-C(19)-H(19-2)	113	3
C(3)-C(2)-H(2-1)	109	2	C(18)-C(19)-H(19-3)	120	7
C(3)-C(2)-H(2-2)	110	1	H(19-1)-C(19)-H(19-2)	87	6
H(2-1)-C(2)-H(2-2)	109	2	H(19-1)-C(19)-H(19-3)	94	8
C(2)-C(3)-H(3)	109	1	H(19-2)-C(19)-H(19-3)	122	7
C(4)-C(3)-H(3)	105	1	C(3)-O(1)-H(O)	105	3
O(1)-C(3)-H(3)	106	1			

$C(17)H_3$; this shows that the acetolysis of II proceeds with an inversion of the configuration at the C(14) atom. Thus, Compound IV can be fully expressed by the name: *d,l*-1,1,4aα-trimethyl-2α-hydroxy-8α-acetoxy-1,2,3,4,4a,5,6,7,8,9-decahydrophenanthrene.

The torsion angles for the tricyclic system are given in Fig. 2. The A and B rings take, respectively, distorted chair and boat forms very similar to those found in III.[2] On the other hand, the C ring has the ordinary half-chair form, which is nearly as puckered

Table 5. The intramolecular H···H contacts (Å)

	D	σ		D	σ
H(1-1)···H(2-1)	2.34	0.03	H(6)···H(7-2)	2.29	0.05
H(1-2)···H(2-1)	2.31	0.05	···H(15-3)	2.14	0.06
···H(2-2)	2.36	0.04	H(7-2)···H(14)	2.39	0.05
···H(11-1)	2.23	0.05	H(11-1)···H(12-2)	2.37	0.06
H(2-1)···H(3)	2.39	0.04	···H(17-3)	2.21	0.04
···H(O)	2.33	0.06	H(11-2)···H(12-1)	2.34	0.07
H(2-2)···H(16-3)	2.30	0.04	H(12-1)···H(13-1)	2.40	0.05
···H(17-1)	2.25	0.05	H(13-1)···H(14)	2.36	0.05
···H(O)	2.34	0.07	H(13-2)···H(14)	2.21	0.04
			H(16-3)···H(17-1)	2.09	0.06

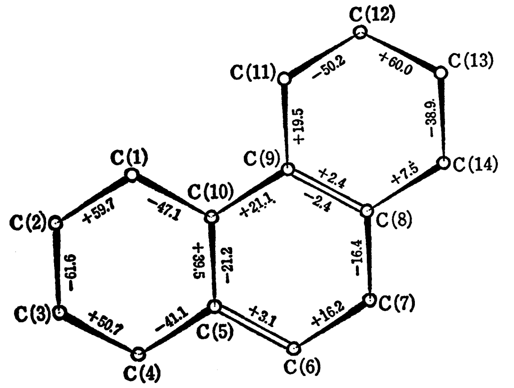

Fig. 2. The torsion angles (°) for the tricyclic system.

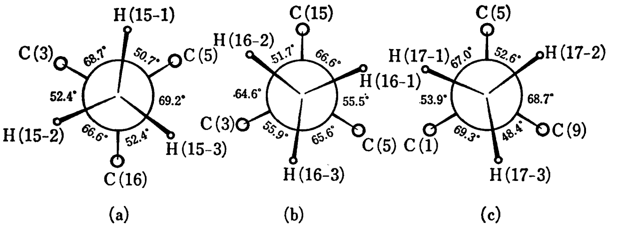

Fig. 3. The Newman projections along the bonds, (a) C(4)-C(15), (b) C(4)-C(16), and (c) C(10)-C(17).

as those in many other cyclohexene derivatives. The acetoxyl group, like the methoxyl group in III, is axially oriented by the flipping of the C ring, although the configuration at the C(14) atom is inverted. The bond lengths and angles calculated with the final coordinates are listed in Tables 3 and 4 respectively. These values are all reasonable, considering their estimated standard deviations. Table 5 gives the intramolecular H···H distances smaller than 2.40 Å.

It may be said that the A ring in the present molecule is still less puckered than that in III, because the average torsion angle for the former, 50.0°, is about 2.2° smaller than that for the latter. Out of the corresponding torsion angles in these two rings, those around the C(3)-C(4), C(4)-C(5), and C(5)-C(10) bonds especially differ by about 4° to 6°. These differences may be attributable partly to the replacement of the benzoyl group with the hydrogen atom, but seem to arise mainly from the flipping of the C ring. Considering the fact that, in IV, the hydrogen atoms attached to the C(1) and C(11) atoms keep distances of at least 2.23 Å without any great distortion of the C ring, the flipping of the C ring would remarkably lessen the steric repulsion between the A and C rings. Consequently, the two axial methyl groups, C(16)H_3 and C(17)H_3, would be allowed to become somewhat more distant from each other by the conformational change in the A and B rings. In fact, as may be seen in Fig. 3, the deviations of the C(16)H_3 and C(17)H_3 groups from the staggered conformation, 6° and 8°, are somewhat smaller than the corresponding values for III, 13° and 10° respectively, although the H(16—3) and H(17—1) atoms keep a distance of about 2.09 Å, which is nearly equal to that in III, 2.05 Å. On the contrary, the C(15)H_3 group is forced to rotate by about 8° from the staggered arrangement, so that the H(15–3) atom may be separated at a distance of about 2.14 Å from the H(6) atom. This rotation angle is about 5° larger than the corresponding angle for III. The O(1)-H(O) bond takes approximately the eclipsed conformation with the C(2)-C(3) bond, the deviation being about 14°. This conformation seems to be caused by the hydrogen-bond formation of the hydroxyl group with the acetyl oxygen atom of another molecule, O(3′). Because of the unstable eclipsed conformation of the hydroxyl group, the angle between the O(1)-H(O) and O(1)···O(3′) directions is reduced to about 12°. It is interesting to notice that the alternate valence angles in the A ring are significantly larger than the usual tetrahedral angle. This may show a way in which a cyclohexene ring is distorted by forming an exocyclic double bond.

The conformation of the B ring is almost symmetrical with respect to the plane which approximately bisects the C(6)-C(7)-C(8) and C(5)-C(10)-C(9) angles. The two nonconjugated double bonds in the ring, C(5)=C(6) and C(8)=C(9), are both twisted to some extent. The deviations of the atoms from the least-squares best planes through the C(4), C(5), C(6), C(7), and C(10) atoms and through the C(7), C(8), C(9), C(10), C(11), and C(14) atoms are given in Table 6. The two planes make a dihedral angle of about 20°; this is about 5° larger than the corresponding angle for III.

In the present molecule, the C ring does not show the unusual behavior found in III.[2] The thermal motions of the C(12) and C(13) atoms as well as the bond distances and angles related to these atoms are normal,as

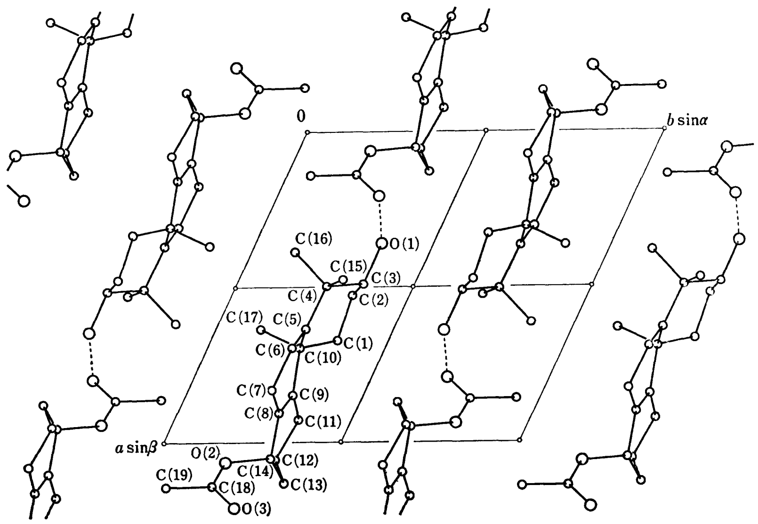

Fig. 4. The molecular arrangement viewed along the c axis.

TABLE 6. THE DEVIATIONS OF THE ATOMS FROM THE LEAST-SQUARES PLANES

Plane I		Plane II	
Atom	Deviation, Å	Atom	Deviation, Å
C(4)	0.000	C(7)	−0.003
C(5)	0.013	C(8)	−0.002
C(6)	−0.013	C(9)	0.020
C(7)	0.006	C(10)	−0.007
C(8)[a]	0.440	C(11)	−0.008
C(9)[a]	0.462	C(12)[a]	−0.525
C(10)	−0.006	C(13)[a]	0.206
H(6)[a]	−0.07	C(14)	−0.001

a) The atoms indicated with asterisks were omitted from the calculations of the least-squares planes.

TABLE 7. THE SHORT INTERMOLECULAR DISTANCES (Å)
The standard deviations are given in parentheses.

(1) I···II (III···I)		(5) I···IX (IX···I)	
C(12)···O(1)	3.429(4)	C(6)···C(16)	3.848(3)
C(13)···O(1)	3.447(4)	C(7)···C(16)	3.791(3)
C(18)···C(15)	3.978(4)	(6) I···X (X···I)	
(2) I···IV (V···I)		C(11)···C(11)	3.875(4)
O(3)···C(12)	3.758(5)	(7) I···XI (XI···I)	
C(15)···C(2)	3.684(3)	O(2)···C(19)	3.709(4)
(3) I···VI (VII···I)		C(17)···C(19)	3.971(6)
O(3)···C(2)	3.489(3)	(8) I···XII (XII···I)	
···O(1)	2.881(3)	C(6)···C(13)	3.825(3)
(4) I···VIII (VIII···I)			
C(17)···C(17)	3.715(3)		

I: x/a, y/b, z/c (given in Table 2). II: $1+x/a, y/b, z/c$. III: $-1+x/a, y/b, z/c$. IV: $x/a, y/b, 1+z/c$. V: $x/a, y/b, -1+z/c$. VI: $1+x/a, y/b, 1+z/c$. VII: $-1+x/a, y/b, -1+z/c$. VIII: $1-x/a, -y/b, -z/c$. IX: $1-x/a, -y/b, 1-z/c$. X: $2-x/a, 1-y/b, -z/c$. XI: $2-x/a, -y/b, 1-z/c$. XII: $2-x/a, 1-y/b, 1-z/c$.

compared with those in III. The C ring has a somewhat unsymmetrical half-chair form, the displacements of the C(12) and C(13) atoms from the mean plane through the C(8), C(9), C(11), and C(14) atoms being 0.51 and 0.22 Å respectively. The sum of these deviations, 0.73 Å, is in good agreement with that in cyclohexene, 0.7346 Å.[4] The distance between the H(1-2) and H(11-1) atoms is about 2.23 Å; this is nearly equal to the H(1-2)···H(11-2) distance in III, 2.17 Å. As has already been mentioned, the acetoxyl group in the present molecule, like the methoxyl group in III, takes the axial orientation. The fact that, independently of the configuration at the C(14) atom, the C ring has a half-chair conformation with these axially-oriented groups implies that such a conformation may be the preferred one of a cyclohexene ring which has a methoxyl or an acetoxyl group at the allylic position. It is also of interest that the internal valence angles of the sp^3 type at the C(11) and C(14) atoms, 113.1° and 114.8°, lie between those of the sp^2 type at the C(9) and C(8) atoms, 120.8° and 123.0°, and those of the sp^3 type at the C(12) and C(13) atoms, 109.5° and 111.0°, respectively. This may show a typical distribution of strains in a cyclohexene ring. The acetyl group is located at such a position that the torsion angles, O(3)–C(18)–O(2)–C(14) and C(18)–O(2)–C(14)–H(14), are about −3.4° and −15° respectively. Consequently, the O(3) atom is very close to the H(14) atom; the distance between them is only about 2.30 Å. This close contact suggests that the negatively-charged carbonyl oxygen atom and the more or less positively-charged hydrogen atom may exert quite strong attractive forces on each other.

The molecular arrangement viewed along the c axis is shown in Fig. 4. The short intermolecular distances are also given in Table 7. The molecules are connected by an intermolecular hydrogen bond, O(1)···O(3′), at a distance of 2.881 Å, forming a linear chain parallel to [101]. These molecular chains are further held together mainly by the usual van der Waals interactions.

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[4] J. F. Chiang and S. H. Bauer, *J. Amer. Chem. Soc.*, **91**, 1898 (1969).