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4,4-Dimethyl Effect. (4). The Conformation of α-Onoceradienedione in the Crystalline State[1]

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Single crystals of α-onoceradienedione grown in methanol are orthorhombic, $a=7.897$, $b=26.299$, $c=6.281$ Å, $U=1304.5$ Å^3, $D_c=1.117$ g/cm^3, $Z=2$ with space group $P2_12_12$. The structure, solved by the use of the MULTAN program, revealed that ring A (and also ring D) of the compound has a flattened chair conformation, the dihedral angle of 4β-methyl and the carbonyl plane being 97°.

Keywords——α-onoceradienedione; 4,4-dimethyl-3-keto-$\Delta^{8(14)}$-steroid ring A conformation; 4,4-dimethyl effect; X-ray analysis; flattened chair conformation

In the course of studies on the 4,4-dimethyl effect in 4,4-dimethyl-3-keto steroids possessing a double bond at various positions in ring B, our attention was attracted to the abnormal (ORD) of α-onoceradienedione, a $\Delta^{8(26)}$-compound, which showed a considerable bathochromic shift of the peak and though compared to the curves expected for normal 4,4-dimethyl-3-keto steroids.[2] The abnormality is more clearly apparent in the circular dichroism (CD) spectrum, which gives a double humped curve with a negative maximum at 305 nm ($\Delta\varepsilon=-0.341$) and a positive maximum at 272 nm ($\Delta\varepsilon=0.116$) in MeOH, while in dioxane the curve changes to negative peaks (λ_{max} 306 nm, $\Delta\varepsilon=-0.603$) (see Fig. 1). The pattern contrasts remarkably with the negative curves of Δ^7-compounds[3] (ring A is a chair form)[4] and the positive curves of Δ^5-compounds[3] (ring A is a twist-boat form),[5] and rather resembles those of Δ^8-compounds[3] (ring A conformation is not firmly established).[6] The above abnormality is not attributable to the mutual interactions between 3-ketone and 8(26)-double bond, because they are too far apart to interact significantly.

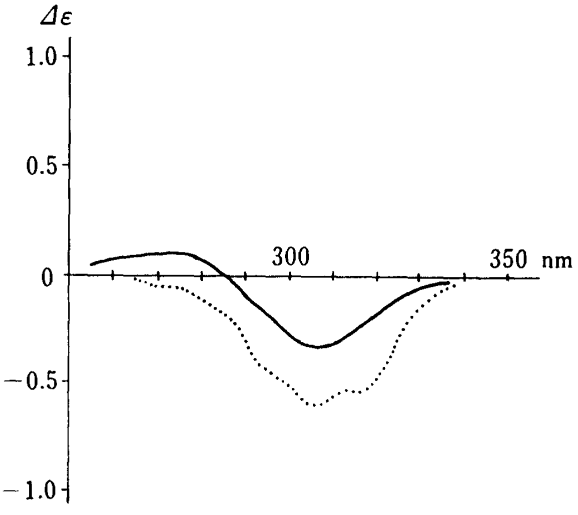

Fig. 1. CD Spectra of α-Onoceradienedione
——, in MeOH; ······, in dioxane.

Theoretically such a double humped curve might be the sum of two opposite CD spectra with the maxima at slightly different positions.[7] However, there is no reason to assume that the two halves of α-onoceradienedione have different CD contributions due to conformational dissymmetry. Thus, the above abnormality may be attributed to an inherent conformational property of ring A (and also ring D) of the compound.

We therefore decided to carry out X-ray analysis of the compound to obtain precise information on the conformation of ring A (and also ring D), at least in the crystalline state.

Experimental

Crystallographic Measurements——Single crystals of α-onoceradienedione were grown in methanol as colorless prisms. A computer-controlled Philips PW-1100 four-circle X-ray autodiffractometer was used

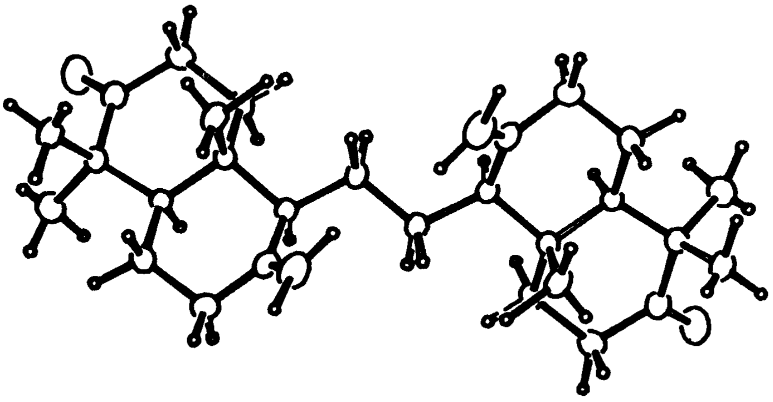

Fig. 2. A Perspective Drawing of the Molecule of α-Onoceradienedione

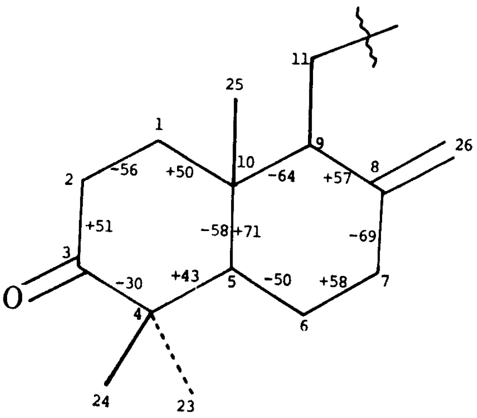

Fig. 3. Endo-cyclic Torsional Angles (°) of α-Onoceradienedione

TABLE I. Positional Parameters with Their Estimated Standard Deviations and Equivalent Isotropic Thermal Parameters of α-Onoceradoenedione

Atom	X ($\times 10^4$)	Y ($\times 10^4$)	Z ($\times 10^4$)	Beq (Å^2)
C1	3695 (3)	645 (1)	1279 (6)	3.67 (0.04)
C2	5425 (4)	885 (1)	810 (7)	4.59 (0.05)
C3	5310 (4)	1448 (1)	293 (5)	3.75 (0.04)
C4	4130 (3)	1780 (1)	1601 (5)	3.10 (0.03)
C5	2505 (3)	1487 (1)	2320 (4)	2.72 (0.03)
C6	1441 (4)	1797 (1)	3904 (6)	4.14 (0.04)
C7	−286 (4)	1545 (1)	4281 (7)	4.08 (0.05)
C8	−32 (4)	1002 (1)	4961 (5)	3.78 (0.04)
C9	914 (3)	692 (1)	3303 (5)	3.06 (0.03)
C10	2749 (3)	923 (1)	3076 (4)	2.79 (0.03)
C11	898 (3)	115 (1)	3672 (6)	3.84 (0.04)
C23	3579 (5)	2233 (1)	187 (7)	5.11 (0.05)
C24	5195 (4)	1997 (1)	3443 (6)	4.17 (0.04)
C25	3709 (4)	865 (1)	5180 (5)	4.02 (0.04)
C26	−493 (5)	838 (2)	6854 (6)	5.48 (0.05)
O	6188 (4)	1623 (1)	−1107 (5)	6.09 (0.04)

Atom	X ($\times 10^3$)	Y ($\times 10^3$)	Z ($\times 10^3$)	Beq (Å^2)
HC1	377 (5)	27 (1)	157 (6)	4.6 (0.8)
H′C1	278 (6)	65 (2)	−43 (8)	6.6 (1.1)
HC2	630 (6)	68 (2)	−14 (8)	7.6 (1.2)
H′C2	618 (5)	87 (1)	231 (7)	5.1 (0.8)
HC5	174 (5)	145 (1)	92 (6)	4.8 (0.8)
HC6	209 (5)	182 (1)	546 (6)	4.7 (0.8)
H′C6	145 (5)	220 (1)	343 (7)	5.6 (0.9)
HC7	−107 (6)	160 (2)	309 (7)	7.3 (1.1)
H′C7	−90 (6)	173 (1)	528 (8)	6.9 (1.1)
HC9	24 (5)	77 (1)	176 (6)	4.3 (0.7)
HC11	162 (3)	−7 (1)	258 (4)	2.9 (0.6)
H′C11	174 (5)	4 (2)	506 (6)	5.7 (0.9)
HC23	462 (5)	235 (1)	−33 (5)	4.6 (0.7)
H′C23	284 (6)	251 (1)	97 (7)	6.2 (1.1)
H″C23	260 (6)	211 (2)	−121 (8)	7.5 (1.2)
HC24	558 (4)	181 (1)	429 (6)	4.7 (0.7)
H′C24	625 (4)	216 (1)	299 (6)	4.3 (0.8)
H′C24	439 (6)	224 (2)	451 (8)	7.7 (1.1)
HC25	393 (7)	40 (2)	555 (9)	9.1 (1.3)
H′C25	311 (5)	106 (1)	643 (3)	6.0 (0.9)
H″C25	476 (5)	93 (1)	506 (6)	5.2 (0.8)
HC26	−10 (6)	46 (1)	745 (6)	5.4 (0.8)
H′C26	−112 (5)	109 (1)	798 (7)	5.6 (0.9)

for all measurements. The intensities of all the reflections in the range of 6° through 156° in 2θ angles were measured using the θ—2θ scan method with a scan speed of 6°/min in θ. Of the total of 1658 reflections measured by the use of monochromated Cu-$K\alpha$ radiation, 1483 had intensities above the $2\sigma(I)$ level and they were used for the structure determination.

Crystal Data——$C_{30}H_{46}O_2$, $M=438.7$. Orthorhombic, $a=7.897(8)$, $b=26.299(26)$, $c=6.281(6)$ Å, $U=1304.5$ Å^3, $D_c=1.117$ g/cm^3, $Z=2$; $\mu(\mathrm{Cu}-K\alpha)=4.81$ cm^{-1}. Space group $P2_12_12$.

Structure Analysis and Refinement——The structure was solved by the direct method using MULTAN[8] and refined by the block-diagonal least-squares method to an R value of 0.058. All the hydrogen atoms were located on the difference electron-density map and they were included in the least-squares refinement with isotropic temperature factors.

TABLE II. Interatomic Distances (Å), with Standard Deviations in Parentheses

C 1	−C 2	1.534 (4)
C 1	−C10	1.538 (4)
C 2	−C 3	1.520 (4)
C 3	−C 4	1.519 (4)
C 3	−O	1.210 (4)
C 4	−C 5	1.563 (3)
C 4	−C23	1.549 (4)
C 4	−C24	1.540 (4)
C 5	−C 6	1.537 (4)
C 5	−C10	1.569 (3)
C 6	−C 7	1.535 (4)
C 7	−C 8	1.504 (4)
C 8	−C 9	1.516 (4)
C 8	−C26	1.317 (5)
C 9	−C10	1.576 (3)
C 9	−C11	1.541 (3)
C10	−C25	1.532 (4)
C11	−C11	1.541 (4)

TABLE III. Bond Angles (°), with Standard Deviations in Parentheses

C 2	−C 1	−C10	112.2 (2)
C 3	−C 2	−C 1	112.9 (3)
C 4	−C 3	−C 2	118.8 (3)
C 4	−C 3	−O	121.7 (3)
C 2	−C 3	−O	119.5 (3)
C 5	−C 4	−C 3	112.1 (2)
C 5	−C 4	−C23	108.4 (2)
C 5	−C 4	−C24	114.5 (2)
C 3	−C 4	−C23	107.7 (2)
C 3	−C 4	−C24	106.5 (2)
C23	−C 4	−C24	107.4 (2)
C 6	−C 5	−C 4	112.0 (2)
C 6	−C 5	−C10	111.9 (2)
C 4	−C 5	−C10	117.0 (2)
C 7	−C 6	−C 5	110.9 (3)
C 8	−C 7	−C 6	109.6 (3)
C 9	−C 8	−C 7	112.2 (3)
C 9	−C 8	−C26	125.5 (3)
C 7	−C 8	−C26	122.1 (3)
C10	−C 9	−C 8	108.1 (2)
C10	−C 9	−C11	113.5 (2)
C 8	−C 9	−C11	114.9 (2)
C25	−C10	−C 1	110.2 (2)
C25	−C10	−C 5	114.5 (2)
C25	−C10	−C 9	109.9 (2)
C 1	−C10	−C 5	106.6 (2)
C 1	−C10	−C 9	109.4 (2)
C 5	−C10	−C 9	106.1 (2)
C11	−C11	−C 9	113.2 (2)

Result and Discussion

The result of X-ray analysis shows that α-onoceradienedione has a diad rotation axis: that is, each half of the molecule makes exactly the same contribution to the CD spectrum. Therefore, the abnormality of its CD should be attributed to the conformational properties of ring A (and also ring D) itself. The endocyclic torsional angles indicate that ring A (and also ring D) of the compound has a distorted chair conformation, which is more distorted than the ring A of Δ^7-compounds.[4] The dihedral angle between 4β-methyl and the carbonyl plane[9] is 97°, the value being about intermediate between those of chair (~120°) and flat (sofa) forms (~60°).

We consider that the anomalous CD of α-onoceradienedione is a result of the flattening of ring A. This may be formally expressed in terms of equilibration of chair (~75%) and boat (~25%) forms. Detailed discussion of this point will be presented in a forthcoming publication.

References and Notes

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