BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (3), 935—936 (1978)

# The Crystal and Molecular Structure of 4-(1-Hydroxy-2,6,6-trimethyl-2-cyclohexenyl)-3-buten-2-one

Hideo UEDA,* Chuji KATAYAMA, and Jiro TANAKA

*Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464*

(Received August 26, 1977)

**Synopsis.** The crystal and molecular structure of a hydroxy derivative of α-ionone, 4-(hydroxy-2,6,6-trimethyl-2-cyclohexenyl)-3-buten-2-one, was studied by means of X-ray analysis. The atoms including the conjugated double bond in the side chain and those around the double bond in the ring form planes orthogonal to each other.

4-(1-Hydroxy-2,6,6-trimethyl-2-cyclohexenyl)-3-buten-2-one is an important derivative of (—)-α-ionone in its correlation to the structure of abscisic acid. Oritani and Yamashita have synthesized the optical active compounds[1-3] and provided us with crystals for X-ray analysis. The structure is interesting from the view point of CD analysis of α-ionone and abscisic acid.

## Experimental

The space group of the crystal determined from the oscillation and Weissenberg photographs. The unit-cell parameters were determined by the least-squares method, using 12 reflections carefully measured on Hilger & Watts four-circle diffractometer with Ni-filtered Cu $K\alpha$ radiation($\lambda$=1.5418 Å). Crystal data: $C_{13}H_{20}O_2$, $M.W.$=208.30, orthorhombic $P2_12_12_1$, $a$=12.359(1), $b$=13.018(1), $c$=7.738(1) Å, Z=4, $D_m$=1.109, $D_c$=1.111 g·cm$^{-3}$, $\mu$=5.84 cm$^{-1}$ (for Cu $K\alpha$ radiation). The intensity data were collected on a diffractometer with $2\theta$-$\omega$ scanning mode($2\theta \leqq 72°$). The size of the crystal used was 0.3×0.3×0.3 mm. An isotropic extinction correction was made by the method of Hamilton.[4]

## Determination and Refinement of the Structure

The structure was determined by the direct method with the program MULTAN[5] using 127 reflections with $|E| \geqq 1.50$. An E map computed from the phase set with the highest figures of merit (FOM=1.21) revealed all the atoms except those of hydrogen. Refinement of the structure was performed by the block-diagonal least-squares method with 1152 independent reflections of $|F^\circ| \geqq 3\sigma$. The final refinement was carried out with anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal factors for hydrogen atoms. The $R$-index converged to 0.053 with an equal weight for each reflection. The atomic scattering factors were taken from the International Tables for X-ray Crystallography.[6] Part of the computation was performed at the Nagoya University Computation Center. The observed and calculated structure factors are given in Table 1.[7]

* Present address: Central Research Laboratory, Ube Industries Ltd., Nishihon-machi, Ube, Yamaguchi 755.

TABLE 2. ATOMIC COORDINATES AND THEIR STANDARD DEVIATIONS

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| C (1) | 0.0536 (3) | 0.8926 (3) | 0.9609 (4) |
| C (2) | 0.1308 (3) | 0.8007 (3) | 0.9945 (5) |
| C (3) | 0.2411 (4) | 0.8216 (4) | 0.9133 (6) |
| C (4) | 0.2932 (3) | 0.9186 (4) | 0.9788 (6) |
| C (5) | 0.2147 (3) | 1.0037 (4) | 1.0023 (5) |
| C (6) | 0.1081 (3) | 0.9941 (3) | 0.9993 (5) |
| C (7) | 0.0828 (5) | 0.7009 (4) | 0.9167 (8) |
| C (8) | 0.1466 (4) | 0.7864 (4) | 1.1909 (6) |
| C (9) | 0.0338 (4) | 1.0853 (4) | 1.0305 (6) |
| C (10) | 0.0217 (3) | 0.8979 (3) | 0.7726 (5) |
| C (11) | −0.0794 (3) | 0.9023 (3) | 0.7125 (5) |
| C (12) | −0.1001 (3) | 0.9092 (3) | 0.5239 (5) |
| C (13) | −0.2165 (4) | 0.9079 (5) | 0.4670 (6) |
| O (1) | −0.0271 (3) | 0.9173 (3) | 0.4205 (3) |
| O (2) | −0.0450 (2) | 0.8810 (2) | 1.0569 (3) |
| H (O2) | −0.038 (3) | 0.889 (3) | 1.141 (5) |
| H (C3a) | 0.237 (3) | 0.822 (3) | 0.796 (5) |
| H (C3b) | 0.300 (3) | 0.759 (3) | 0.934 (5) |
| H (C4a) | 0.319 (4) | 0.903 (4) | 1.093 (7) |
| H (C4b) | 0.346 (4) | 0.951 (4) | 0.888 (7) |
| H (C5) | 0.255 (4) | 1.073 (3) | 1.010 (6) |
| H (C7a) | 0.081 (3) | 0.701 (3) | 0.794 (6) |
| H (C7b) | 0.133 (4) | 0.630 (4) | 0.948 (7) |
| H (C7c) | −0.014 (4) | 0.706 (4) | 0.943 (7) |
| H (C8a) | 0.071 (3) | 0.760 (3) | 1.246 (6) |
| H (C8b) | 0.173 (4) | 0.849 (4) | 1.246 (7) |
| H (C8c) | 0.206 (4) | 0.729 (4) | 1.205 (7) |
| H (C9a) | −0.031 (4) | 1.088 (4) | 0.936 (7) |
| H (C9b) | −0.013 (4) | 1.064 (4) | 1.156 (7) |
| H (C9c) | 0.078 (5) | 1.166 (4) | 1.023 (8) |
| H (C10) | 0.091 (3) | 0.902 (3) | 0.685 (5) |
| H (C11) | −0.154 (4) | 0.897 (3) | 0.791 (6) |
| H (C13a) | −0.226 (4) | 0.923 (3) | 0.354 (6) |
| H (C13b) | −0.253 (4) | 0.835 (4) | 0.487 (7) |
| H (C13c) | −0.278 (5) | 0.946 (4) | 0.551 (8) |

## Results and Discussion

The structure is shown in Fig. 1. The atomic coordinates for all atoms are given in Table 2. Intramolecular distances and bond angles are all normal. The atoms of side chain, C(10), C(11), C(12), C(13), and O(1), are on the plane $0.0300X-0.9961Y-0.0829Z+1.075=0$, where the maximum deviation is 0.03 Å. The double bonds C(10)=C(11) and C(12)=O(1) take a *cis* conformation. The atoms around the C(5)=C(6) double bond in the ring also form a plane given by $0.0157X+0.2309Y-0.9789Z-1.801=0$, where the

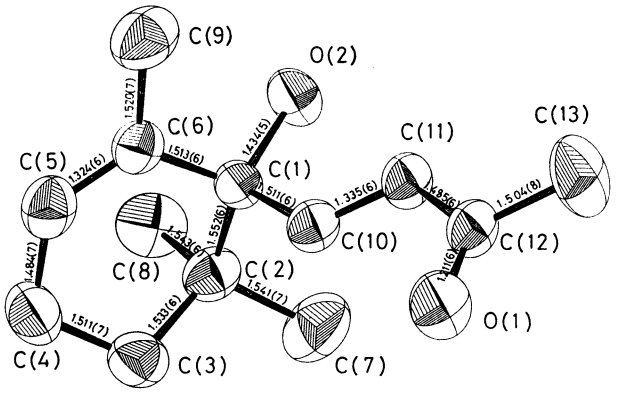


Fig. 1. The atomic labelings of (−)-1′-hydroxy-α-ionone.
Carbon and oxygen atoms are represented as thermal ellipsoids of a size such that the vibrating atoms have a 50% probability of being found within them. The absolute configuration of the melecule was drawn to be in conformity with the established configuration by a chemical correlation method.

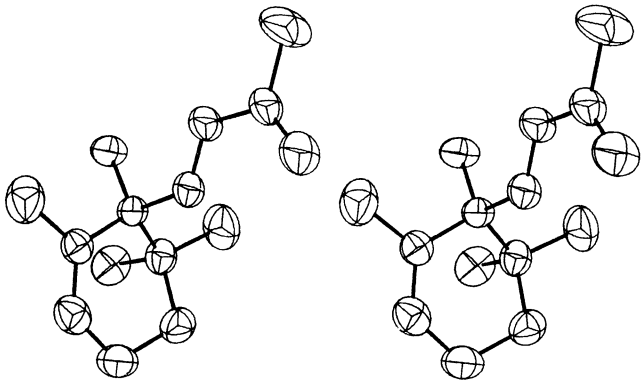

Fig. 2. A stereoscopic view of (−)-1′-hydroxy-α-ionone.
The absolute configuration and the criterion to the thermal ellipsoids of carbon and oxygen atoms are the same as in Fig. 1.

maximum deviation is 0.02 Å. These planes are at an angle of 97° to each other. A stereoscopic view of

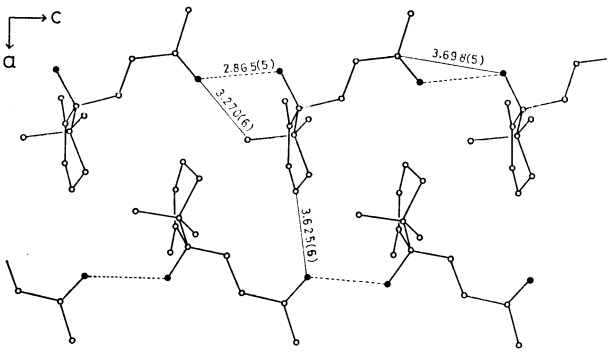


Fig. 3. The projection of molecules along the b axis.
Carbon atoms are depicted as open circles and oxygen atoms as filled circles. Hydrogen bonds are represented with broken lines. The configuration is the same as in Fig. 1.

the molecule is shown in Fig. 2, and the projection of molecules in the crystal in Fig. 3. Hydrogen bonding exists between the oxygen atoms of the carbonyl group of the side chain and the hydroxyl group of the adjacent molecule. All the other interatomic contacts are normal.

The authors are grateful to Dr. Takayuki Oritani, Tohoku University, for supply of the sample.

## References

1) T. Oritani and K. Yamashita, *Agric. Biol. Chem.*, **36**, 885(1972).
2) T. Oritani and K. Yamashita, *Tetrahedron Lett.*, **1972**, 2521.
3) T. Oritani and K. Yamashita, *Agric. Biol. Chem.*, **37**, 1115(1973).
4) W.C. Hamilton, *Acta Crystallogr.*, **10**, 629(1957).
5) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368(1971).
6) "International Tables for X-Ray Crystallography," Birmingham, Vol III, Kynoch Press (1968), p. 201.
7) Table 1 is kept at the Chemical Society of Japan, Kanda, Surugadai, Chiyoda-ku, Tokyo (Document No. 7808).