**Discussion.** The final positional parameters and equivalent isotropic temperature factors for the non-H atoms are given in Table 1.* Interatomic distances are in Table 2. A normal projection of the molecule with the atomic numbering is shown in Fig. 1, while a clinographic projection of the unit cell showing the molecular packing is given in Fig. 2. The two five-membered dihydroisoxazole and cyclopentane rings form an angle of 103·7 (4)°. The bonding of the two bridged C atoms C(1) and C(7) approximates to $sp^3$ hybridization. The dichlorophenyl ring is planar to within 0·04 Å. The two five-membered rings deviate considerably from planarity. The cycloheptanone ring has a chair conformation, which is energetically more stable than that of the boat alternative with torsion angles comparable to those in 2-bromodihydroisophoto-α-santonic lactone acetate (Asher & Sim, 1965). The mean plane of the cycloheptanone ring almost bisects the angle of the planes of the two five-membered rings, forming with them angles of 114·2 (4) and 138·4 (3)°. Owing to the C=O and C=N double bonds, the geometries around C(2) and C(8) are $sp^2$. The plane of the dichlorophenyl ring is almost perpendicular, 84·8 (3)°, to the plane of the dihydroisoxazole ring due to the strain caused by the interaction between the carbonyl group and the *o*-Cl-substituted phenyl ring. All bond lengths and angles are in good agreement with accepted values.

Thanks are due to Professor N. E. Alexandrou for useful suggestions and to the University of Thessaloniki for the use of its computing facilities.

---

* Lists of structure amplitudes, anisotropic thermal parameters, coordinates and isotropic temperature factors for H atoms, bond angles, least-squares-plane calculations and selected torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43672 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

### References

Asher, J. D. M. & Sim, G. A. (1965). *J. Chem. Soc.* pp. 1584–1594.

Herr, M. L. (1977). *Tetrahedron*, **33**, 1897–1903.

Ibers, J. A. & Hamilton, W. C. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 71–151. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Ito, T. C. & Sugawara, V. (1983). *Best Plane Program BP70*. Institute of Physical and Chemical Research, RIKEN, Wako, Japan.

Main, P. (1970). *DATRED. A Computer Program for the Reduction of Raw Diffractometer Data to FOBS*. Univ. of York, England.

Main, P., Lessinger, L., Woolfson, M. M., Germain, G. & Declercq, J.-P. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain-la-Neuve, Belgium.

Malamidou-Xenikaki, E., Coutouli-Argyropoulou, E. & Alexandrou, N. (1985). *Tetrahedron Lett.* **26**, 4105–4106.

Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. W. & Hall, S. R. (1972). The *XRAY72* system–version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H. & Flack, H. (1976). The *XRAY76* system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

---

*Acta Cryst.* (1987). C**43**, 1153–1155

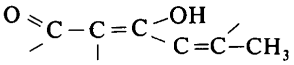
# Structure of (5*RS*,6*RS*)-1,5-Diacetyl-6-benzoxymethyl-2-hydroxy-4-methyl-1,3-cyclohexadiene*

By E. Moreno, S. Perez, A. López-Castro and R. Márquez

*Departamento de Optica y Sección de Física del Departamento de Investigaciones Físicas y Químicas del CSIC, Universidad de Sevilla, Spain*

(*Received* 27 *May* 1986; *accepted* 12 *January* 1987)

**Abstract.** $C_{19}H_{20}O_5$, $M_r = 328·36$, triclinic, $P\bar{1}$, $a = 8·117$ (2), $b = 8·453$ (1), $c = 13·352$ (2) Å, $\alpha = 89·82$ (2), $\beta = 83·24$ (2), $\gamma = 113·38$ (2)°, $V = 833·8$ (3) Å$^3$, $Z = 2$, $D_m = 1·29$, $D_x = 1·30$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu$(Mo $K\alpha$) = 0·108 mm$^{-1}$, $F(000) = 348$, $T = 293$ K, $R = 0·078$ for 2729 observed [$I > 2\sigma(I)$] independent reflections. The cyclohexadiene ring conformation is twist–boat. There is some electron delocalization along the system



$O{=}C{-}C{=}C(OH){-}C{=}C{-}CH_3$

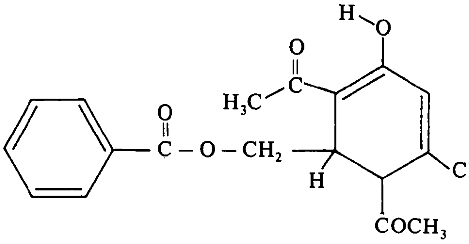
of the diacetylhydroxymethylcyclohexadiene group. The configuration around the chiral centres C(9) and C(11) of the cyclohexadiene ring is *R*,*R*. Packing of the molecules is governed by van der Waals contacts.

---

* [(1*RS*,6*RS*)-2,6-Diacetyl-3-hydroxy-5-methyl-2,4-cyclohexadienyl]methyl benzoate.

**Introduction.** Some 2,4-diacetyl-3-alkyl-5-hydroxy-5-methylcyclohexanes, which are products from the reaction of *O*-alkyl- and *O*-arylglycolaldehydes and 2,4-pentanedione, reacted severally with toluene-*p*-sulfonic acid in benzene to give (5*RS*,6*RS*)-1,5-diacetyl-6-alkyl-2-hydroxy-4-methyl-1,3-cyclohexadienes.

When this reaction was carried out with methyl benzoate the title compound (I), was obtained. This compound has been widely studied by IR, UV and $^1$H NMR (López Aparicio, Zorrilla Benitez, Garcia Mendoza & Sontoyo Gonzalez, 1984) but it was not possible to establish the relative configurations of the chiral centres in the molecule, so an X-ray study was undertaken to investigate the complete geometry.



(I)

**Experimental.** $D_m$ measured by flotation. Single crystal in form of colourless prism with approximate dimensions $0{\cdot}15 \times 0{\cdot}13 \times 0{\cdot}09$ mm used for intensity-data collection; preliminary Weissenberg photographs indicated that the crystals are triclinic with space group $P\bar{1}$. Lattice parameters refined using 25 reflections in the range $3 < \theta < 13°$. Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\omega/2\theta$ mode, $2\theta_{\max} = 60°$ ($h \le 11$, $-10 \le k \le 9$, $-14 \le l \le 18$). Two standard reflections ($2\bar{3}\bar{3}$ and $\bar{2}33$) monitored every 100 reflections showed only statistical fluctuations. From 4847 measured reflections only 2729 were observed with $I > 2\sigma(I)$, $R_{\rm int} = 0{\cdot}030$ from merging 64 equivalent reflections. Lorentz–polarization but no absorption or extinction corrections. Structure solved by direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); 346 $E$ values ($E > 1{\cdot}83$) used as input to *MULTAN*80 and the correct set with the highest figure of merit of 2·876 and residual value of 11·70 gave approximate positions of 20 non-hydrogen atoms. A Fourier map revealed the positions of the other non-hydrogen atoms. Scattering factors from *International Tables for X-ray Crystallography* (1962). Full-matrix least-squares refinement based on $F$ of positional and anisotropic thermal parameters of all non-H atoms and weighting scheme $w = 1/\sigma^2(F)$. A difference Fourier synthesis revealed positions of all H atoms. Further refinement with non-hydrogen atoms treated anisotropically and H atoms isotropically produced convergence with $R = 0{\cdot}078$, $wR = 0{\cdot}078$ and $S = 3{\cdot}8$. The final difference Fourier synthesis showed $\Delta\rho \le 0{\cdot}3$ e Å$^{-3}$, $(\Delta/\sigma)_{\max} = 0{\cdot}002$. The *XRAY* system (Stewart, Kundell & Baldwin, 1970) was used. The high $R$ value obtained is probably attributable to the rather poor quality of the crystal.

**Discussion.** The positional and isotropic thermal parameters are given in Table 1. Bond lengths and angles are given in Fig. 1, which shows a view of the molecule.*

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j a_i^* a_j^* a_i a_j \cos(\mathbf{a}_i.\mathbf{a}_j) \times 10^4.$$

| | $x$ | $y$ | $z$ | $U_{\rm eq}$(Å$^2$) |
|---|---|---|---|---|
| O(1) | 817 (3) | 2851 (3) | 6358 (2) | 428 (9) |
| O(71) | 374 (4) | 2591 (4) | 4736 (2) | 567 (12) |
| O(111) | −4303 (4) | −3512 (3) | 8519 (3) | 581 (12) |
| O(151) | −1529 (4) | −3980 (4) | 7988 (2) | 570 (13) |
| O(181) | −1369 (5) | 1391 (6) | 10143 (2) | 826 (17) |
| C(1) | 3072 (6) | 6022 (5) | 4283 (3) | 472 (15) |
| C(2) | 4530 (6) | 7603 (5) | 4098 (3) | 542 (17) |
| C(3) | 5594 (6) | 8327 (5) | 4836 (3) | 504 (15) |
| C(4) | 5213 (6) | 7474 (5) | 5778 (3) | 514 (16) |
| C(5) | 3757 (5) | 5898 (5) | 5977 (3) | 402 (13) |
| C(6) | 2678 (5) | 5153 (4) | 5226 (3) | 351 (12) |
| C(7) | 1169 (5) | 3414 (4) | 5387 (3) | 364 (12) |
| C(8) | −509 (5) | 1104 (4) | 6589 (2) | 370 (12) |
| C(9) | −534 (4) | 718 (4) | 7711 (2) | 320 (11) |
| C(10) | −1515 (4) | −1213 (4) | 7965 (3) | 352 (11) |
| C(11) | −3347 (5) | −1863 (5) | 8335 (3) | 409 (13) |
| C(12) | −4291 (4) | −736 (5) | 8549 (3) | 400 (12) |
| C(13) | −3399 (4) | 966 (4) | 8571 (3) | 355 (12) |
| C(14) | −1350 (4) | 1789 (4) | 8366 (2) | 351 (11) |
| C(15) | −650 (5) | −2363 (5) | 7796 (3) | 413 (13) |
| C(16) | 1294 (6) | −1792 (6) | 7402 (3) | 524 (17) |
| C(17) | −4349 (6) | 2130 (6) | 8850 (3) | 518 (17) |
| C(18) | −539 (5) | 2135 (6) | 9365 (3) | 481 (15) |
| C(19) | 1367 (7) | 3453 (8) | 9311 (4) | 873 (25) |

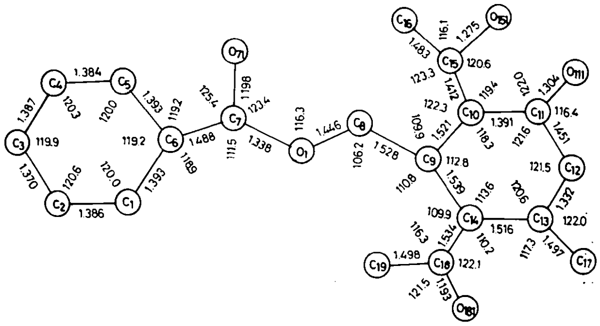


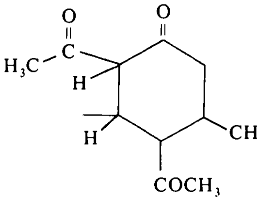
Fig. 1. View of the molecule with atom numbering, bond lengths (Å) and angles (°); e.s.d.'s are 0·003–0·006 Å and 0·3–0·4°.

---

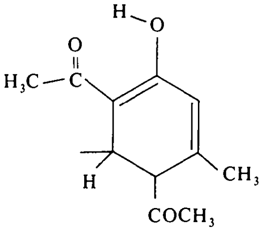
* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43711 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

*Substituted cyclohexadiene group.* There is extensive electron delocalization involving one of the acetyls, the hydroxyl, the methyl and a part of the cyclohexadiene group, as reflected in the molecular dimensions. The C(10)=C(11) bond distance is 1·391 (5) Å which is much longer than the C=C bond in ethylene [1·336 (2) Å] (Bartell, Roth, Hollowell, Kuchitsu & Young, 1965). The C(15)=O(151) bond distance of 1·275 (4) Å is also longer than the C=O bond in the acetyl groups which shows that this carbonyl group is affected by some electron delocalization; also it is involved in an intramolecular hydrogen bond, O(111)–H···O(151) = 2·642 (5) Å.

The other carbonyl bond C(18)–O(181) is 1·193 (4) Å. There is a shortening of the C(11)–O(111) bond, 1·304 (4) Å, which is shorter than the 1·36 (1) Å reported for the O–$C_{sp^2}$ bond (*International Tables for X-ray Crystallography*, 1962). The C(10)–C(15) and C(11)–C(12) lengths of 1·412 (6) and 1·451 (6) Å respectively are shorter than the 1·487 (5) Å reported for the $C_{sp^2}$–$C_{sp^2}$ single bond (Shmueli, Shanan-Atidi, Horwitz & Shvo, 1973). It has been suggested that the molecule could be represented by one of the two forms

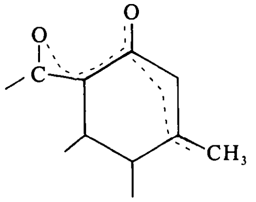


(II)



(III)

(López Aparicio, Zorrilla Benitez, Garcia Mendoza & Santoyo Gonzalez, 1984). These authors concluded from IR, $^1$H NMR and UV spectroscopy that the compound exists as form (III) in the solid state. The present investigation fully confirms formula (III), although there is extensive delocalization, represented by



The cyclohexadiene conformation is approximately twist-boat with asymmetry parameters (Nardelli, 1983) $C_2$[C(10)] = 0·066 and $C_s$[C(9)–C(14)] = 0·017°. C(10),C(11),C(12),C(13),C(16) and C(17) are roughly in a plane and O(111) and C(15) deviate from the plane by −0·22 and −0·11 Å respectively. The Newman projections (Fig. 2) show that the chiralities of the C(9) and C(14) atoms are *R*,*R*.

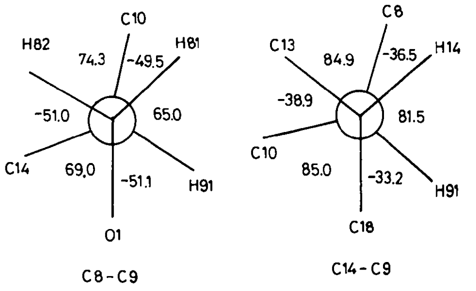


Fig. 2. Two Newman projections concerning chiral centers. Torsion angles in °; e.s.d.'s are in the range 0·3–0·6° (excluding those involving H atoms).

*Benzoxymethyl group.* This group displays normal geometry. Average distances and angles for the phenyl ring are 1·393 (4) Å and 120·0 (1)° respectively. This group is approximately planar except for the O(71) atom. The main torsion angles are: C(5)–C(6)–C(7)–O(71) = −168·0 (4), C(1)–C(6)–C(7)–O(71) = 9·0 (6), C(6)–C(7)–O(1)–C(8) = −174·3 (3) and C(7)–O(1)–C(8)–C(9) = 174·8 (3)°.

*Molecular packing.* There is only one intermolecular distance less than 3·4 Å involving non-H atoms, C(16)···O(71)(−*x*,−*y*,−*z* + 1) = 3·261 (6) Å. The molecules are held in the crystal by van der Waals forces.

The authors thank Professor López Aparicio for supplying the crystals. The present work is a part of a wider research project supported by the Government through the Comisión Asesora de Investigación Científica y Técnica.

### References

BARTELL, L. C., ROTH, E. A., HOLLOWELL, C. D., KUCHITSU, K. & YOUNG, J. E. (1965). *J. Chem. Phys.* **42**, 2683–2686.

*International Tables for X-ray Crystallography* (1962). Vol. III, pp. 202–207, 275–276. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

LÓPEZ APARICIO, F. J., ZORRILLA BENITEZ, F., GARCIA MENDOZA, P. & SONTOYO GONZALEZ, F. (1984). *An. Quím.* **80**, 295–300.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

NARDELLI, M. (1983). *Acta Cryst.* C**39**, 1141–1142.

SHMUELI, U., SHANAN-ATIDI, H., HORWITZ, H. & SHVO, Y. (1973). *J. Chem. Soc. Perkin Trans* 2, pp. 657–662.

STEWART, J. M., KUNDELL, F. & BALDWIN, J. C. (1970). The *XRAY* system. Computer Science Center, Univ. of Maryland, College Park, Maryland.