Acta Cryst. (1987). C**43**, 571–572

The Structure of 4-(2,4-Dihydroxy-2,6,6-trimethylcyclohexylidene)-3-buten-2-one

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(*Received* 22 *August* 1986; *accepted* 20 *October* 1986)

Abstract. $C_{13}H_{20}O_3$, $M_r = 224{\cdot}3$, orthorhombic, $Pna2_1$, $a = 25{\cdot}94$ (1), $b = 7{\cdot}804$ (5), $c = 6{\cdot}890$ (5) Å, $U = 1394{\cdot}78$ Å^3, $Z = 4$, $D_m = 1{\cdot}03$, $D_x = 1{\cdot}07$ g cm^{-3}, Cu $K\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å, $\mu = 5{\cdot}30$ cm^{-1}, $F(000) = 488$, $T = 293$ K, $R = 0{\cdot}069$ for 641 unique reflections. The two hydroxyl groups are *trans* to one another. The secondary hydroxyl group occupies an equatorial position. Bond lengths and angles are normal; the allene angle is 179·5 (13)°.

Introduction. The title compound was isolated from a froth produced as a defensive mechanism by the flightless grasshopper *Romalea microptera* (Meinwald, Erickson, Hartshorn, Meinwald & Eisner, 1968). In this and a further paper (Meinwald & Hendry, 1969) it was concluded that the compound was an allenic sesquiterpene with the structural formula shown in Fig. 1. This study confirms this conclusion.

Experimental.* Refined cell dimensions measured on a Pailred diffractometer. The data were collected with Cu $K\alpha$ monochromatized radiation (graphite crystal) from a crystal mounted along the c axis. 1863 independent reflections measured within one quadrant, 641 unique observed reflections on merging Friedel pairs. Absorption corrections not applied. Structure solved by direct methods with *MITHRIL* (Gilmore, 1983) using E values obtained from *SHELX*76 (Sheldrick, 1976). Refinement (on F) by full-matrix least squares using *SHELX*76. H-atom positions included at calculated positions based on peak positions on a difference Fourier map. Non-hydrogen atoms refined anisotropically. H atoms included as fixed atoms with isotropic temperature factor of 0·1 Å^2. 144

* The authors apologize for the lack of detail concerning the experimental conditions of the data collection. The data were collected by Fleischer in 1969 and the outputs containing the relevant details have become lost in the intervening years. An $hk0$ projection $R \sim 20\%$ was obtained in 1969 but no success was achieved in three dimensions. The data were sent by Fleischer to Tollin in 1969 as 641 observed reflections and an unsuccessful attempt to solve the structure using Patterson methods was made. The advent of *MITHRIL* was the key which unlocked the door.

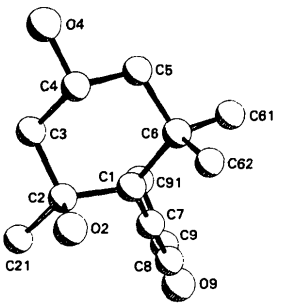

Fig. 1. View of molecule showing conformation and atomic numbering.

Table 1. *Coordinates* ($\times 10^4$) *for non-hydrogen atoms and equivalent isotropic thermal parameters* (Å$^2 \times 10^3$) *with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
C1	8831 (3)	3003 (13)	4086 (19)	30 (3)
C2	9077 (3)	1192 (13)	3792 (19)	33 (3)
C21	8730 (4)	22 (14)	2575 (22)	50 (4)
O2	9573 (2)	1387 (9)	2852	38 (2)
C3	9184 (4)	374 (13)	5782 (22)	38 (3)
C4	9503 (4)	1553 (14)	7090 (19)	40 (3)
O4	9601 (3)	734 (11)	8953 (15)	53 (2)
C5	9181 (4)	3174 (13)	7530 (20)	42 (4)
C6	9070 (4)	4222 (13)	5671 (22)	41 (4)
C61	8679 (4)	5630 (15)	6190 (25)	62 (5)
C62	9559 (4)	5080 (15)	4785 (23)	59 (4)
C7	8455 (4)	3495 (16)	2966 (24)	54 (4)
C8	8084 (5)	3992 (18)	1872 (25)	80 (6)
C9	7528 (5)	3865 (23)	2350 (32)	102 (8)
C91	7382 (5)	3204 (21)	4281 (35)	94 (7)
O9	7198 (4)	4227 (21)	1158 (29)	180 (8)

Table 2. *Interatomic distances* (Å)

C2–C1	1·564 (14)	C5–C4	1·546 (14)
C6–C1	1·575 (15)	C6–C5	1·547 (17)
C7–C1	1·302 (15)	C61–C6	1·537 (15)
C21–C2	1·532 (15)	C62–C6	1·559 (15)
O2–C2	1·447 (11)	C8–C7	1·281 (17)
C3–C2	1·537 (15)	C9–C8	1·483 (18)
C4–C3	1·530 (15)	C91–C9	1·476 (25)
O4–C4	1·456 (13)	O9–C9	1·220 (18)

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parameters refined, $R = 0.069$, $wR = 0.070$, unit weights. Max. Δ/σ 0.01, max. difference map peak 0.22, min. −0.24 e Å^{-3}. In view of the high temperature factors for atoms C91 and O9 [largest values O9: U_{33} 0.247 Å^2, U_{22} 0.203 Å^2; C91: U_{33} 0.146 Å^2] the electron density in the vicinity was examined closely for indications of statistical disorder of these atoms. There were no such indications. Other programs used were *XANADU* (Roberts & Sheldrick, 1975) and *PLUTO* (Motherwell & Clegg, 1978). Scattering factors from *International Tables for X-ray Crystallography* (1974). No correction for secondary extinction.

Discussion. Atomic numbering is shown in Fig. 1. Atomic coordinates of the non-hydrogen atoms are given in Table 1,* with bond lengths in Table 2. There are two hydrogen bonds in the structure both involving O2 and O4. O4···O2($2-x$, $-y$, $\frac{1}{2}+z$) 2.81 (2) Å and O2···O4(x, y, $-1+z$) 2.74 (2) Å. O9 is not involved in any close contacts. The cyclohexane ring has a chair conformation. Fig. 2 is a view of the unit cell showing hydrogen bonding.

The authors wish to thank Dr J. Meinwald for supplying the compound and for his continuing interest.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43504 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

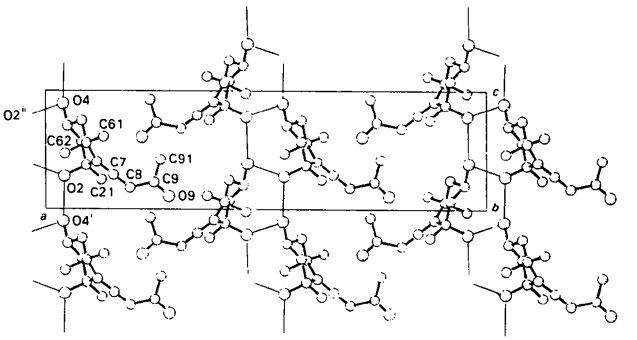

Fig. 2. View of unit cell along b showing hydrogen bonding as thin lines. Symmetry codes: (i) x, y, $-1+z$; (ii) $2-x$, $-y$, $\frac{1}{2}+z$.

References

GILMORE, C. J. (1983). *MITHRIL. A Computer Program for the Automatic Solution of Crystal Structures from X-ray Data.* Univ. of Glasgow, Scotland.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

MEINWALD, J., ERICKSON, K., HARTSHORN, M., MEINWALD, Y. C. & EISNER, T. (1968). *Tetrahedron Lett.* **25**, 2959–2962.

MEINWALD, J. & HENDRY, L. (1969). *Tetrahedron Lett.* **21**, 1657–1660.

MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO.* Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

ROBERTS, P. & SHELDRICK, G. M. (1975). *XANADU.* Program for crystallographic calculations. Univ. of Cambridge, England.

SHELDRICK, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1987). C**43**, 572–577

Molecular Structure Analysis of Benzamide Neuroleptics and Analogs. XI. *exo*-2,3-Dihydro-*N*-(8-benzyl-8-azabicyclo[3.2.1]oct-3-yl)-1,3-benzodioxole-5-carboxamide and *exo*-2,3-Dihydro-*N*-(8-benzyl-8-azabicyclo[3.2.1]oct-3-yl)-1,4-benzodioxin-4-carboxamide

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(*Received* 4 *September* 1986; *accepted* 20 *October* 1986)

Abstract. (I) $C_{22}H_{24}N_2O_3$. $M_r = 364.4$, monoclinic, $P2_1/n$, $a = 12.833$ (5), $b = 12.012$ (6), $c = 12.515$ (5) Å, $\beta = 101.12$ (3)°, $V = 1893.0$ Å^3, $Z = 4$, $D_x = 1.28$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.49$ cm^{-1}, $F(000) = 776$, $R = 0.04$ for 1720 reflections. (II) $C_{22}H_{25}N_2O_3^+.Cl^-.H_2O$. $M_r = 418.9$, monoclinic, $P2_1/c$, $a = 15.580$ (1), $b = 6.865$ (1), $c = 19.928$ Å, $\beta = 104.85$ (1)°, $V = 2060.2$ Å^3, $Z = 4$, $D_x = 1.35$ g cm^{-3}, λ(Cu $K\alpha$) = 1.54178 Å, $\mu = 17.94$ cm^{-1}, $F(000) = 888$, $R = 0.04$ for 1929 reflections. (III) $C_{23}H_{26}N_2O_3$. $M_r = 378.5$, monoclinic, $P2_1/n$, $a = 12.994$ (3), $b = 12.435$ (3), $c = 12.417$ (4) Å, β

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