

## Structural Investigation of Highly Hindered Methanol Derivatives. 2. The Structure of $\alpha,\alpha$ -Dicyclohexylcyclohexanemethanol

BY PAOLO SGARABOTTO\* AND FRANCO UGOZZOLI

*Istituto di Strutturistica Chimica, Università degli Studi di Parma, Centro di Studio per la Strutturistica  
Diffraattometrica del CNR, Viale delle Scienze, I-43100 Parma, Italy*

SALVATORE SORRISO

*Dipartimento di Chimica, Università di Perugia, I-06100 Perugia, Italy*

AND ZBIGNIEW MALARSKI

*Instytut Chemii, Uniwersytet Wrocławski, 50–383 Wrocław, Poland*

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**Abstract.**  $C_{19}H_{34}O$ ,  $M_r = 278.5$ , triclinic,  $P\bar{1}$ ,  $a = 10.910$  (2),  $b = 9.529$  (2),  $c = 9.305$  (2) Å,  $\alpha = 115.8$  (1),  $\beta = 86.8$  (1),  $\gamma = 96.7$  (1)°,  $V = 865.0$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.07$  g cm<sup>-3</sup>,  $Cu K\alpha$ ,  $\lambda = 1.5418$  Å,  $\mu = 4.4$  cm<sup>-1</sup>,  $F(000) = 312$ ,  $T = 293$  K, final conventional  $R = 0.046$  for 2314 independent observed reflections. The cyclohexane rings adopt a highly symmetric chair conformation. The hydrogen bonds involving the oxygen atoms of two centrosymmetric molecules lead to the formation of centrosymmetric dimers.

**Introduction.** The crystal structure determination of the title compound was undertaken in continuation of our studies on the molecular dynamics of alcohols (Sgarabotto, Ugozzoli, Sorriso & Malarski, 1988). Previous papers (Malarski, Szostak & Sorriso, 1984, 1987) described the infrared and Raman spectra for tricyclohexylcarbinol in the temperature range 10–380 K (IR) and 120–380 K (R). From these measurements an equilibrium between monomers and dimers was suggested for the liquid state just as in the case of a solution in an inert solvent. The experimental results indicate that the two components of the doublet of the  $\nu(OH)_{free}$  band observed in the liquid state became a singlet in the crystalline state. The frequency corresponding to the maximum observed in the solid state lies just between the two values measured in the liquid state. Moreover the unequivocal establishment of the crystal and molecular structure of this compound allows a better interpretation of the experimental results obtained with other techniques.

**Experimental.** Colourless prismatic crystals elongated along [001] obtained by slow crystallization from cyclohexane. Siemens AED diffractometer on-line to a

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters (Å<sup>2</sup>  $\times 10^4$ ) for non-hydrogen atoms with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}$
O(1)	680 (1)	6321 (1)	9775 (2)	467 (5)
C(1)	1886 (1)	6067 (2)	9030 (2)	372 (6)
C(11)	2780 (1)	6061 (2)	10275 (2)	378 (6)
C(12)	2543 (2)	4618 (2)	10623 (2)	461 (7)
C(13)	3459 (2)	4641 (2)	11811 (2)	539 (8)
C(14)	3481 (2)	6133 (2)	13364 (2)	592 (9)
C(15)	3724 (2)	7568 (2)	13042 (3)	616 (8)
C(16)	2791 (2)	7542 (2)	11870 (2)	493 (7)
C(21)	1697 (1)	4442 (2)	7554 (2)	406 (6)
C(22)	2865 (2)	3842 (2)	6599 (3)	525 (9)
C(23)	2591 (3)	2147 (3)	5339 (3)	743 (10)
C(24)	1532 (3)	1971 (3)	4243 (3)	811 (11)
C(25)	398 (2)	2617 (3)	5189 (3)	718 (10)
C(26)	686 (2)	4306 (2)	6415 (3)	564 (9)
C(31)	2276 (1)	7404 (2)	8484 (2)	401 (6)
C(32)	3674 (1)	7857 (2)	8448 (2)	441 (6)
C(33)	3997 (2)	9046 (2)	7779 (2)	547 (8)
C(34)	3329 (2)	10498 (2)	8643 (3)	618 (9)
C(35)	1943 (2)	10060 (2)	8644 (3)	658 (10)
C(36)	1608 (2)	8879 (2)	9332 (3)	586 (9)

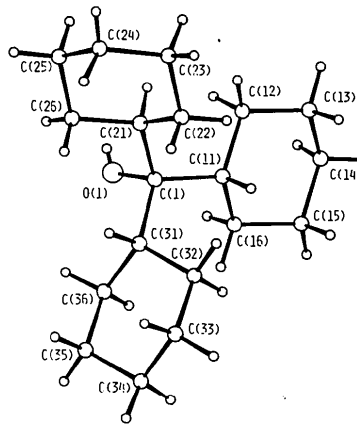


Fig. 1. Perspective view of the molecule showing the atomic numbering scheme.

\* To whom all correspondence should be addressed.

Table 2. Bond distances (Å) and angles (°) with e.s.d.'s in parentheses

O(1)—C(1)	1.448 (2)	C(21)—C(26)	1.528 (3)
C(1)—C(11)	1.557 (3)	C(22)—C(23)	1.533 (3)
C(1)—C(21)	1.560 (3)	C(23)—C(24)	1.530 (5)
C(1)—C(31)	1.573 (3)	C(24)—C(25)	1.506 (4)
C(11)—C(12)	1.535 (3)	C(25)—C(26)	1.521 (3)
C(11)—C(16)	1.539 (3)	C(31)—C(32)	1.538 (2)
C(12)—C(13)	1.523 (3)	C(31)—C(36)	1.529 (3)
C(13)—C(14)	1.522 (3)	C(32)—C(33)	1.514 (3)
C(14)—C(15)	1.514 (3)	C(33)—C(34)	1.514 (3)
C(15)—C(16)	1.523 (4)	C(34)—C(35)	1.521 (3)
C(21)—C(22)	1.530 (3)	C(35)—C(36)	1.521 (4)
O(1)—C(1)—C(11)	107.5 (2)	C(1)—C(21)—C(26)	114.4 (3)
O(1)—C(1)—C(21)	104.9 (3)	C(22)—C(21)—C(26)	109.4 (2)
O(1)—C(1)—C(31)	107.8 (3)	C(21)—C(22)—C(23)	110.4 (4)
C(11)—C(1)—C(21)	112.2 (3)	C(22)—C(23)—C(24)	112.0 (3)
C(11)—C(1)—C(31)	113.3 (3)	C(23)—C(24)—C(25)	111.3 (2)
C(21)—C(1)—C(31)	110.6 (2)	C(24)—C(25)—C(26)	111.2 (4)
C(1)—C(11)—C(12)	114.2 (2)	C(21)—C(26)—C(25)	111.0 (3)
C(1)—C(11)—C(16)	113.0 (3)	C(1)—C(31)—C(32)	115.4 (3)
C(12)—C(11)—C(16)	108.5 (2)	C(1)—C(31)—C(36)	115.4 (2)
C(11)—C(12)—C(13)	112.4 (3)	C(32)—C(31)—C(36)	110.0 (3)
C(12)—C(13)—C(14)	112.1 (3)	C(31)—C(32)—C(33)	112.9 (3)
C(13)—C(14)—C(15)	110.7 (2)	C(32)—C(33)—C(34)	112.3 (2)
C(14)—C(15)—C(16)	111.2 (3)	C(33)—C(34)—C(35)	110.6 (3)
C(11)—C(16)—C(15)	112.5 (3)	C(34)—C(35)—C(36)	112.1 (4)
C(1)—C(21)—C(22)	115.6 (3)	C(31)—C(36)—C(35)	112.6 (3)
O(1)—C(1)—C(11)—C(12)	70.4 (4)	C(12)—C(11)—C(16)—C(15)	55.7 (5)
O(1)—C(1)—C(11)—C(16)	-54.3 (4)	C(11)—C(12)—C(13)—C(14)	55.4 (5)
C(21)—C(1)—C(11)—C(12)	-44.5 (5)	C(12)—C(13)—C(14)—C(15)	-54.6 (5)
C(21)—C(1)—C(11)—C(16)	-169.2 (3)	C(13)—C(14)—C(15)—C(16)	55.1 (5)
C(31)—C(1)—C(11)—C(12)	-170.6 (3)	C(14)—C(15)—C(16)—C(11)	-57.2 (5)
C(31)—C(1)—C(11)—C(16)	64.7 (4)	C(1)—C(21)—C(22)—C(23)	171.8 (4)
O(1)—C(1)—C(21)—C(22)	-176.5 (4)	C(26)—C(21)—C(22)—C(23)	-57.2 (5)
O(1)—C(1)—C(21)—C(26)	54.9 (4)	C(1)—C(21)—C(26)—C(25)	-169.5 (4)
C(11)—C(1)—C(21)—C(22)	-60.1 (5)	C(22)—C(21)—C(26)—C(25)	58.9 (5)
C(11)—C(1)—C(21)—C(26)	171.3 (3)	C(21)—C(22)—C(23)—C(24)	55.1 (5)
C(31)—C(1)—C(21)—C(22)	67.5 (4)	C(22)—C(23)—C(24)—C(25)	-53.6 (5)
C(31)—C(1)—C(21)—C(26)	-61.1 (5)	C(23)—C(24)—C(25)—C(26)	54.5 (5)
O(1)—C(1)—C(31)—C(32)	151.0 (4)	C(24)—C(25)—C(26)—C(21)	-57.9 (5)
O(1)—C(1)—C(31)—C(36)	20.9 (5)	C(1)—C(31)—C(32)—C(33)	175.0 (3)
C(11)—C(1)—C(31)—C(32)	32.1 (5)	C(36)—C(31)—C(32)—C(33)	-52.4 (5)
C(11)—C(1)—C(31)—C(36)	-97.9 (4)	C(1)—C(31)—C(36)—C(35)	-174.8 (4)
C(21)—C(1)—C(31)—C(32)	-94.8 (4)	C(32)—C(31)—C(36)—C(35)	52.6 (5)
C(21)—C(1)—C(31)—C(36)	135.1 (4)	C(31)—C(32)—C(33)—C(34)	54.4 (5)
C(1)—C(11)—C(12)—C(13)	178.5 (3)	C(32)—C(33)—C(34)—C(35)	-54.5 (5)
C(16)—C(11)—C(12)—C(13)	-54.5 (4)	C(33)—C(34)—C(35)—C(36)	54.8 (5)
C(1)—C(11)—C(16)—C(15)	-176.6 (3)	C(34)—C(35)—C(36)—C(31)	-55.1 (5)

General Automation Jumbo 220 microcomputer, Ni-filtered Cu *K*α radiation,  $\theta$ - $2\theta$  scan, scan width from  $(\theta-0.60)^\circ$  to  $(\theta+0.60+0.142\tan\theta)^\circ$ ; scan speed  $3.0^\circ \text{ min}^{-1}$ . Crystal dimensions  $0.19 \times 0.29 \times 0.52 \text{ mm}$ . Cell dimensions based on 29  $(\theta, \chi, \phi)_{hkl}$  measured intensities, 3186 symmetry-independent reflections ( $-13 \leq h \leq 13$ ,  $-10 \leq k \leq 10$ ,  $0 \leq l \leq 10$ ,  $3 \leq \theta \leq 70^\circ$ ) collected at  $T = 293 \text{ K}$  with a modified version (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) procedure. One standard reflection every 50, no significant variation. Correction for Lorentz and polarization, no correction for absorption effects.

Structure solved by direct methods (SHELX76; Sheldrick, 1976). 2314 observed reflections [ $I > 2\sigma(I)$ ], refinement with full-matrix least squares blocked to 219 and 99 variables corresponding to dicyclohexyl carbinol and cyclohexyl moieties respectively; all H atoms located in the difference Fourier map refined iso-

Table 3. Puckering and asymmetry parameters of the cyclohexyl moieties

Puckering parameters	Ring	Ring	Ring
	C(11)—C(16)	C(21)—C(26)	C(31)—C(36)
$q_2$ (Å)	0.015 (5)	0.038 (4)	0.012 (3)
$q_3$ (Å)	0.567 (6)	0.576 (4)	0.548 (3)
$Q_T$ (Å)	0.567 (6)	0.577 (4)	0.548 (3)
$\theta$ (°)	1.5 (5)	3.7 (4)	1.3 (3)
Asymmetry parameters			
$\Delta C_1$ (C1)	0.008 (3)	0.009 (2)	0.004 (2)
$\Delta C_1$ (C2)	0.009 (3)	0.026 (2)	0.006 (2)
$\Delta C_1$ (C3)	0.003 (3)	0.016 (2)	0.010 (2)
$\Delta C_2$ (C1)	0.249 (2)	0.254 (1)	0.241 (1)
$\Delta C_2$ (C2)	0.248 (2)	0.253 (1)	0.240 (1)
$\Delta C_2$ (C3)	0.248 (2)	0.253 (1)	0.240 (1)
$\Delta C_3$ (C1—C2)	0.314 (2)	0.320 (2)	0.304 (2)
$\Delta C_3$ (C1—C6)	0.314 (2)	0.321 (2)	0.304 (2)
$\Delta C_3$ (C2—C3)	0.314 (2)	0.320 (2)	0.304 (2)
$\Delta C_3$ (C1—C2)	0.008 (2)	0.016 (2)	0.003 (2)
$\Delta C_3$ (C1—C6)	0.005 (2)	0.004 (2)	0.006 (2)
$\Delta C_3$ (C2—C3)	0.005 (2)	0.020 (2)	0.007 (2)

Puckering and asymmetry parameters were calculated by use of the general program system written by Nardelli (1983).

tropically.  $\sum w(|F_o| - |F_c|)^2$  minimized with  $w = [\sigma^2(F_o) + 0.005F_o^2]^{-1}$ ; SHELX76 system (Sheldrick, 1976); maximum shift of parameters  $0.6\sigma$  for O,  $0.5\sigma$  for C,  $1.1\sigma$  for H;  $\Delta\rho_{\text{max}} = 0.16$ ,  $\Delta\rho_{\text{min}} = -0.21 \text{ e } \text{Å}^{-3}$ .

Final refinement converged to  $R = 0.046$ ,  $wR = 0.051$ . Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

**Discussion.** Final atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.\*

A drawing of the molecule with the arbitrary numbering scheme is shown in Fig. 1. Bond distances and angles reported in Table 2 are in good agreement with those found in the related  $\alpha$ -cyclohexylcyclohexanemethanol (Sgarabotto, Ugozzoli, Sorriso & Malarski, 1988) and are as expected for  $C(sp^3)$ - $C(sp^3)$  hybridization; also the conformations of the cyclohexane rings are similar and very close to the chair conformation. The puckering amplitudes (Cremer & Pople, 1975) and the asymmetry parameters (Duax, Weeks & Rohrer, 1976) reported in Table 3 indicate that the cyclohexane moieties all adopt a high degree of symmetry comparable with that found in the analogue dicyclohexylcarbinol (Sgarabotto, Ugozzoli, Sorriso & Malarski, 1988). The molecular packing is determined by a hydrogen bond of the type  $O-H \cdots O$  [O(1)···O(1<sup>i</sup>) 2.94 (1), H(1)···O(1<sup>i</sup>) 2.38 (5) Å, O(1)—H(1)···O(1<sup>i</sup>) 168.4 (1.5)°; (i) =  $-x, 1-y, 2-z$ ] which

\* 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 44581 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

causes the formation of centrosymmetric dimers. Other contacts are consistent with van der Waals interactions.

## References

- BELLETTI, D., UGOZZOLI, F., CANTONI, A. & PASQUINELLI, G. (1979). *Gestione on line di Diffratometro a Cristallo singolo Siemens AED con sistema General Automation Jumbo 220*. Internal reports 1-3/79. Centro di Studio per la Strutturistica Diffattometrica del CNR, Parma, Italy.
- CREMER, D. & POPLER, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354-1358.
- DUAX, W. L., WEEKS, C. M. & ROHRER, D. C. (1976). *Top. Stereochem.* **9**, 271-385.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* **A30**, 580-589.
- MALARSKI, Z., SZOSTAK, R. & SORRISO, S. (1984). *Lett. Nuovo Cimento*, **40**, 261-264.
- MALARSKI, Z., SZOSTAK, R. & SORRISO, S. (1987). *J. Mol. Struct.* In the press.
- NARDELLI, M. (1983). *PARST. A System of Computer Routines for Calculating Molecular Structure Parameters from the Results of Crystal Structure Analysis. Comput. Chem.* **7**, 95-98.
- SGARABOTTO, P., UGOZZOLI, F., SORRISO, S. & MALARSKI, Z. (1988). *Acta Cryst.* **C44**, 671-673.
- SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

*Acta Cryst.* (1988). **C44**, 676-678

## Structure of Visnagin, 4-Methoxy-7-methyl-5H-furo[3,2-g][1]benzopyran-5-one

BY KARIMAT EL-SAYED

*Physics Department, Faculty of Science, Ain Shams University, Cairo, Egypt*

HERMAN L. AMMON

*Department of Chemistry and Biochemistry and Center for Advanced Research in Biotechnology, University of Maryland, College Park, MD 20742, USA*

AND A. M. ABD EL-RAHMAN

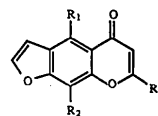
*Physics Department, Faculty of Science, Ain Shams University, Cairo, Egypt*

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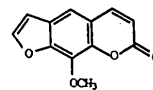
**Abstract.**  $C_{13}H_{10}O_4$ ,  $M_r = 230.22$ , orthorhombic,  $P2_12_12_1$ ,  $a = 7.0870$  (6),  $b = 9.917$  (1),  $c = 14.884$  (2) Å,  $V = 1046$  (1) Å<sup>3</sup>,  $D_x = 1.462$  Mg m<sup>-3</sup> for  $Z = 4$ ,  $\mu = 0.118$  mm<sup>-1</sup>,  $F(000) = 480$ ,  $T = 294$  K, diffractometer data,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å, 1109 data, 817 with  $I > 3\sigma(I)$ ,  $R = 0.031$ . The furobenzopyranone skeleton of the molecule is planar with r.m.s. deviation 0.032 Å. The methoxy methyl group is 1.16 Å out of plane. There are no short intermolecular contacts.

**Introduction.** *Ammi visnaga*, a perennial herbaceous plant that belongs to the family Umbelliferae, grows in the wastelands of the eastern Mediterranean and in the Nile delta. It is one of the more important Egyptian medicinal plants. The seeds have been used since ancient times as a diuretic and as an aid in passing urethral stones. Furobenzopyranones extracted from the seeds, namely visnagin (I), khellin (II) and khellol glucoside (III), have been the object of extensive chemical, pharmacological and clinical research (Huttrer & Dale, 1951). In this paper the structure of

visnagin is reported and compared with the structures of khellin, butocrolol hydrochloride (IV) and xanthotoxin (V).



- (I):  $R_1 = \text{OCH}_3$ ,  $R_2 = \text{H}$ ,  $R_3 = \text{CH}_3$   
 (II):  $R_1 = R_2 = \text{OCH}_3$ ,  $R_3 = \text{CH}_3$   
 (III):  $R_1 = \text{OCH}_3$ ,  $R_2 = \text{H}$ ,  $R_3 = \text{CH}_2\text{-}\beta\text{-glucosyloxy}$   
 (IV):  $R_1 = \text{OH}$ ,  $R_2 = \text{O-CH}_2\text{-CH(OH)-CH}_2\text{-NH}_2\text{-C(CH}_3)_3$  Cl<sup>-</sup>



(V)

**Experimental.** Pale yellow needles from ethanol-water,  $0.35 \times 0.30 \times 0.22$  mm crystal, Enraf-Nonius CAD-4 diffractometer, Mo radiation with incident-beam