Proc. Indian Acad. Sci. (Chem. Sci.) Vol. 100, No. 1, February 1988, pp. 39–44.

A novel structure of secondary alcohol derived from (+)-Δ^3-carene with pseudo three-fold symmetry[†]

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MS received 24 September 1987; revised 7 December 1987

Abstract. The crystal structure of $C_{12}OH_{20}$ (1R-6R-4R-2′R-3,7,7-trimethyl-4-(2-hydroxyethyl) bicyclo [4.1.0] hept-2-ene) has been determined by X-ray diffraction. The compound crystallizes in space group $P2_12_12_1$ with $a = 5{\cdot}893(1)$, $b = 22{\cdot}572(2)$, $c = 26{\cdot}164(3)$ Å, $V = 3480{\cdot}3$ Å^3, $Z = 12$. The structure was solved by modified direct methods and refined to an R value of 0·081 for 607 unique reflections. Each asymmetric unit has three molecules which are held together through intermolecular hydrogen bonds resulting in a novel spiral-type arrangement of molecules. The six-membered ring has a half-chair conformation.

Keywords. Novel terpenoid structure; unusual intermolecular hydrogen-bonding; pseudo three-fold symmetry.

1. Introduction

It has been recently shown (Sonawane *et al* 1985) that *cis*-alkylvinylcyclopropanes which are highly prone to homo 1,5 hydrogen shifts (retro-ene reaction) under thermal conditions could effectively be rearranged to the respective cyclopentenes photochemically (photo-VCR) in good yields. This led to the development of a new methodology for the construction of synthetically useful intermediates such as bicyclo [3.2.0] heptanes under extremely mild conditions. In this context, among the substrates investigated the secondary alcohol ($C_{12}OH_{20}$) was the only solid crystalline product whose X-ray analysis is reported here.

2. Experimental

A wide variety of solvent combinations were checked to procure suitable crystals of the secondary alcohol ($C_{12}OH_{20}$). The use of acetone-water mixture (1:1) was found satisfactory. However, it was noticed that the crystals are brittle and undergo sublimation at room temperature.

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3. Crystal data

$C_{12}OH_{20}$, M = 180·3, orthorhombic, space group $P2_12_12_1$, a = 5·893(1), b = 22·572(2), c = 26·164(3) Å, V = 3480·3 Å^3, Z = 12, Dc = 1·02, Dm = 1·03·

Table 1. Atomic co-ordinates (× 10^4) and isotropic thermal parameters for non-hydrogen atoms with e.s.d.'s in parentheses.

	X	*Y*	*Z*	*B*(Å^2)
Molecule A				
O(1)	11512(31)	4451(6)	2503(6)	4·77
C(1)	11264(52)	3605(9)	3763(9)	4·09
C(2)	10608(53)	4082(11)	3329(10)	5·42
C(3)	10904(55)	4699(11)	3589(10)	5·33
C(4)	13045(49)	4806(10)	3848(8)	4·02
C(5)	14133(49)	4252(10)	4098(9)	4·51
C(6)	12820(49)	3710(11)	4092(9)	4·15
C(7)	9690(52)	3070(12)	3775(10)	5·78
C(8)	12238(49)	4026(10)	2881(9)	4·37
C(9)	12365(48)	3403(10)	2639(9)	4·50
C(10)	13334(54)	4761(11)	4420(10)	5·23
C(11)	11487(6)	4677(12)	4789(11)	7·28
C(12)	15208(50)	5144(11)	4667(9)	5·14
Molecule B				
O(1)	14884(32)	4811(20)	1907(6)	4·96
C(1)	14580(45)	6473(10)	1944(9)	3·44
C(2)	13958(50)	5851(10)	1783(9)	4·26
C(3)	13996(52)	5754(10)	1207(9)	4·83
C(4)	16148(49)	5968(10)	954(9)	4·07
C(5)	17132(43)	6502(9)	1214(8)	3·08
C(6)	16016(53)	6797(11)	1648(10)	5·68
C(7)	12997(60)	6768(13)	2279(11)	7·36
C(8)	15702(49)	5422(10)	2041(8)	3·76
C(9)	15725(63)	5502(12)	2628(12)	8·07
C(10)	16323(52)	6546(10)	643(10)	4·65
C(11)	14405(53)	6948(11)	553(10)	5·59
C(12)	18382(54)	6554(11)	281(9)	4·48
Molecule C				
O(1)	8092(28)	4014(6)	1924(6)	4·06
C(1)	7516(44)	3237(10)	692(9)	3·70
C(2)	6891(53)	3413(12)	1223(10)	5·57
C(3)	7009(48)	2839(10)	1562(9)	4·29
C(4)	9180(48)	2449(10)	1500(8)	2·84
C(5)	10212(47)	2457(12)	962(10)	4·93
C(6)	8898(53)	2800(11)	579(9)	4·67
C(7)	6218(58)	3532(12)	235(10)	5·92
C(8)	8882(50)	3812(10)	1437(9)	4·15
C(9)	9299(50)	4353(10)	1091(9)	4·79
C(10)	9105(63)	1879(13)	1186(10)	6·19
C(11)	10850(62)	1426(12)	1362(12)	7·21
C(12)	7002(62)	1666(13)	939(12)	7·34

g cm^{-3} (floatation in aqueous NaCl solution), $F(000) = 1200$, MoKα radiation, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}67\ cm^{-1}$. Crystal dimensions = $0{\cdot}2 \times 0{\cdot}2 \times 0{\cdot}5$ mm; enclosed in a Lindemann capillary, $\theta < 22{\cdot}5°$; h 0 to 6, K 0 to 24 and l 0 to 28.

Unit cell dimensions were derived from a least-squares fit from 22 reflections ($12° < 2\theta < 30°$). Data collection was on Enraf-Nonius CAD-4F-11M diffractometer. Intensity data were collected in $\omega/2\theta$ scan mode with scan speed 1° min^{-1}. The intensity of three reflections (0 6 0, 0 0 8 and 2 0 5) measured every 3600 s showed only 5% intensity variation. Of 2685 reflections measured, only 607 unique reflections were observed ($|Fo| > 3\sigma|Fo|$).

The structure was solved using MULTAN-78 (Main *et al* 1978) with suitable modifications and after a number of trials. Full matrix least-squares refinement of scale factor, position and only isotropic thermal parameters was made (because of insufficient data and poor quality of crystals). The H atoms leaving out that of the OH group were fixed geometrically and were not refined. The final R value is equal to $R = 0{\cdot}085$ with $WR = 0{\cdot}081$, $W = [12{\cdot}0 + 1{\cdot}0|Fo| + 0{\cdot}02|Fo|^2]^{-1}$. No correction was made for absorption. Atomic scattering factors are from *International tables for X-ray crystallography* (1974). LALS (Gantzel *et al* 1961) was used for refinement.

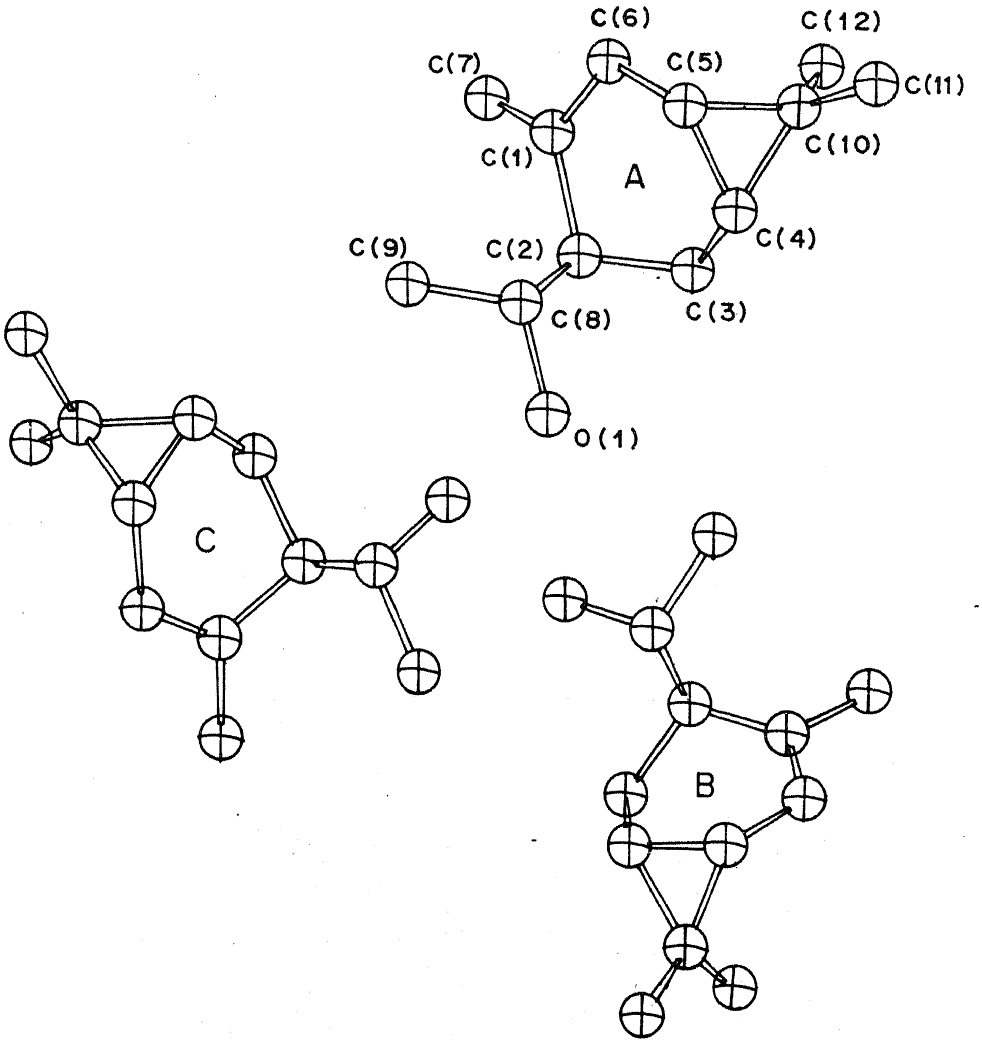

Figure 1. A view of the three molecules in the asymmetric unit (numbering given for molecule A).

4. Discussion

The atomic parameters and their standard deviations for non-hydrogen atoms are given in table 1. Bond lengths and bond angles are given in table 2. Figure 1 shows a perspective view of the molecule along with the numbering of the atoms. Figure 2 shows packing of the molecules down the '*a*' axis.

Substituted Δ^2-carenes are generally found to be either in the liquid or gaseous state and most of the structural results are from electron diffraction studies. Even to obtain crystals of solid alcohol only a 1:1 acetone-water mixture could give suitable crystals for X-ray data collection. However, it was noticed that the crystals undergo slow sublimation at room temperature which necessitated the use of the

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

	Molecule A	*Molecule B*	*Molecule C*
O–C(8)	1·44(3)	1·50(5)	1·43(3)
C(1)–C(2)	1·61(3)	1·51(3)	1·49(4)
C(1)–C(6)	1·28(4)	1·36(4)	1·31(4)
C(1)–C(7)	1·52(4)	1·44(4)	1·57(4)
C(2)–C(3)	1·56(4)	1·53(3)	1·57(4)
C(2)–C(8)	1·52(4)	1·57(4)	1·58(4)
C(3)–C(4)	1·45(4)	1·51(4)	1·56(4)
C(4)–C(5)	1·55(3)	1·50(3)	1·53(3)
C(4)–C(10)	1·51(3)	1·54(3)	1·53(4)
C(5)–C(6)	1·45(4)	1·47(3)	1·48(4)
C(5)–C(10)	1·50(4)	1·57(3)	1·57(4)
C(8)–C(9)	1·54(3)	1·55(4)	1·54(3)
C(10)–C(11)	1·47(4)	1·47(4)	1·52(5)
C(10)–C(12)	1·54(4)	1·54(4)	1·48(5)
C(2)–C(1)–C(6)	121(2)	119(2)	124(2)
C(2)–C(1)–C(7)	114(2)	116(2)	118(2)
C(6)–C(1)–C(7)	125(2)	120(2)	117(2)
C(1)–C(2)–C(3)	105(2)	114(2)	107(2)
C(3)–C(2)–C(8)	110(2)	109(2)	104(2)
C(2)–C(3)–C(4)	117(2)	114(2)	116(2)
C(3)–C(4)–C(5)	115(2)	113(2)	114(2)
C(3)–C(4)–C(10)	123(2)	124(2)	120(2)
C(5)–C(4)–C(10)	59(2)	62(2)	62(2)
C(4)–C(5)–C(6)	117(2)	123(2)	115(2)
C(4)–C(5)–C(10)	59(2)	60(2)	59(2)
C(6)–C(5)–C(10)	119(2)	125(2)	118(2)
C(1)–C(6)–C(5)	123(2)	118(2)	124(2)
O–C(8)–C(2)	107(2)	105(2)	105(2)
O–C(8)–C(9)	110(2)	110(2)	109(2)
C(2)–C(8)–C(9)	115(2)	111(2)	111(2)
C(4)–C(10)–C(5)	62(2)	58(2)	59(2)
C(4)–C(10)–C(11)	125(2)	124(2)	113(2)
C(4)–C(10)–C(12)	117(2)	113(2)	122(3)
C(5)–C(10)–C(11)	120(2)	115(2)	113(2)
C(5)–C(10)–C(12)	116(2)	110(2)	117(3)
C(11)–C(10)–C(12)	109(2)	120(2)	119(3)

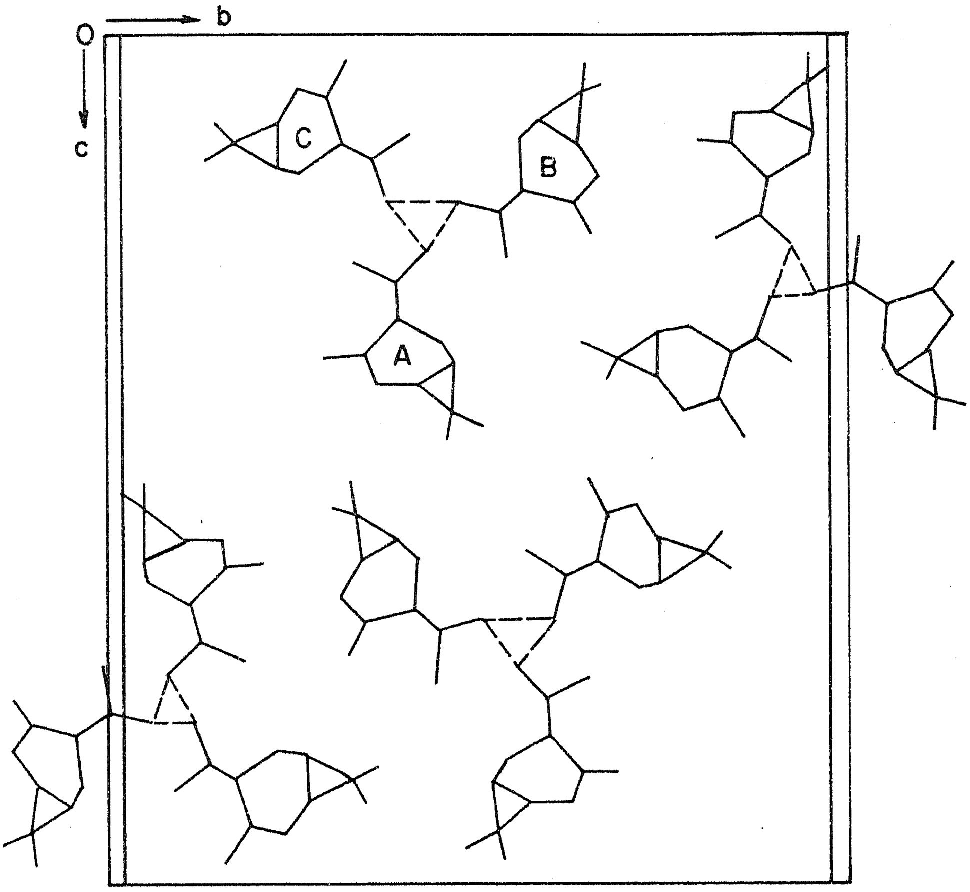

Figure 2. Packing of the molecules (hydrogen bonds indicated by dotted lines) viewed down the *a* axis.

Lindemann capillary. The quality and quantity of data is still poor and has restricted the refinements.

The crystals belong to the space group $P2_12_12_1$ with $Z = 12$ which indicates the presence of three independent molecules in an asymmetric unit, a rather unusual crystal property especially in terpenoids.

With the cell volume $V = 3480{\cdot}3$ Å^3 and a density of about 1.4 g cm^{-3} for a normal organic crystal one gets $Z = 16$. However, the measured crystal density of $D_m = 1.03$ g cm^{-3} gives $Z = 12$ (3 molecules per asymmetric unit). Besides these molecules are uniquely held together in the asymmetric unit by a set of OH ...... O bonds resulting in a pseudo three-fold axis parallel to the *a* direction. Molecule A is bridged by hydrogen bonds to both B and C, while molecule B is hydrogen-bonded to the translated molecule C along the '*a*' axis leading to a spiral type of structure. The average OH ...... O distance is 2·66 Å. The forced three-fold symmetry may also be due to the conformational flexibility of the six-membered ring.

The substituent at C(2) and the three-membered ring are *trans* with respect to each other. The six-membered ring adopts a 'half chair' conformation. The average dihedral angle between the three-membered ring and the plane through C(3), C(4), C(5) and C(6) is 67·6° while it is 77·0° in case of bicyclo [4·1·0]–2–heptene (Hagen and Traetetteberg 1972).

Acknowledgement

We thank Prof. K. Venkatesan, Indian Institute of Science, Bangalore, for providing facilities to do ORTEP plots.

References

Gantzel P K, Sparks R A and Trueblood K N 1961 LALS. A program for the full-matrix least-squares refinement of positional, thermal and scale factors, Univ. of California

Hagen K and Traetetteberg M 1972 *Acta Chem. Scand.* **26** 3636–3642

International tables for X-ray crystallography 1974 (Birmingham: Kynoch Press) vol. 4

Main P, Hull S E, Lessinger L, Germain G, Declercq J P and Woolfson M M 1978 MULTAN–78. A system of computer programs for the automatic solution of crystal structure from X-ray diffraction data, University of York, England, and University of Louvain, Belgium

Sonawane H R, Nanjundiah B S and Udaya Kumar M 1985 *Tetrahedron Lett.* 1097–1100