

Crystal structure analysis of (E)-5,5-dimethyl-3-(4-methylstyryl) cyclohex-2-enone

T. Srinivasan¹, G. Senthilkumar², A. Vadivel²,
H. Manikandan², D.Velmurugan^{1*}

¹CAS in Crystallography and Biophysics, University of Madras, Guindy Maraimalai Campus, Chennai-600025, India

²Department of Chemistry, Annamalai University, Annamalainagar-608002, Tamilnadu, India

*Corres.author: shirai2011@gmail.com

Abstract: The cyclohexanone compound crystallizes in monoclinic $P2_1/n$ space group with four molecules in the asymmetric unit. Crystal data were collected using BRUKER SMART APEX II CCD X-ray diffractometer. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares procedures to the final R_1 of 0.048 using SHELXL programs.

Key Words: cyclohexanone, crystal structure.

Introduction

Cyclohexanone is an aliphatic cyclic ketone. Cyclohexanone derivatives have potent pharmacological activity in the treatment of a broad spectrum of medical conditions¹. The cyclohexanone moiety constitutes an important structural feature in several anti-inflammatory, analgesic, local anesthetic and antihistaminic drugs². In view of its potential applications, the crystal structure determination of the cyclohexanone compound was carried out.

Experimental

X-ray Structure Determination

Single crystal of the compound suitable for x-ray diffraction was obtained by slow evaporation method. Three dimensional intensity data were collected on a Bruker³ SMART APEX CCD Diffractometer using graphite monochromatized Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at CAS in Crystallography and Biophysics, University of Madras, Chennai. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares procedures using the SHELXL programs⁴. All the non-hydrogen atoms were refined using isotropic and later anisotropic thermal parameters. The hydrogen atoms were included in the structure factor calculation at idealized positions by using a riding model, but not refined. Images were created with ORTEP-3⁵. The crystallographic data for the compound are listed in Table 1.

Table 1: Crystal data and structure refinement of the titled compound

Compound	Parameters
Empirical formula	C ₁₇ H ₂₀ O
Formula weight	240.33
Temperature(K)	293(2)
Wavelength(Å)	0.71073
Crystal system, Space group	Monoclinic P2 ₁ /n
Unit cell dimensions a(Å) b(Å) c(Å) β(°)	13.839(5) 6.017(5) 17.808(5) 104.896(5)
Volume(Å ³)	1433.0(2)
Z, D _{cal} (Mgm ⁻³)	4, 1.114
Absorption coefficient (mm ⁻¹)	0.067
F(000)	520
Crystal size(mm)	0.30×0.25×0.20
Theta range for data collection(°)	1.67 to 28.35
Limiting indices	-17<=h<=18, -7<=k<=8, -23<=l<=17
Reflections collected / unique	12706 / 3549
R(int)	0.0310
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3549 / 0 / 167
Goodness-of-fit on F ²	1.028
Final R indices [I>2σ(I)]	R1 = 0.0481, wR2 = 0.1371
R indices (all data)	R1 = 0.0662, wR2 = 0.1558
Largest diff. peak and hole(e.Å ⁻³)	0.194 and -0.169

Synthesis of the compound

A mixture of isophorone (0.01mol), 4-methyl benzaldehyde (0.01mol) and sodium hydroxide solution (10 ml, 10%) in ethanol (25 ml) was stirred at room temperature until the starting material disappeared. The resulting mixture was poured into crushed ice and the precipitate was filtered off, dried and recrystallized from ethanol. Yield: 96%, Mp= 87°C.

Results and Discussion

The cyclohexene ring (C1—C6) adopts an envelope conformation with atom C3 as the flap: puckering parameters⁶ are $Q = 0.443(2)\text{Å}$, $\theta = 53.3(2)^\circ$, and $\varphi = 110.6(2)^\circ$. Its mean plane makes a dihedral angle of $6.00(1)^\circ$ with the benzene ring (C9—C14). The methyl groups C16 and C17 attached with the cyclohexene ring deviate by $-0.2358(3)\text{Å}$ and $1.8176(3)\text{Å}$, respectively. The methyl group C15 attached with the benzene ring deviates by $0.0080(3)\text{Å}$. The molecule adopts an extended conformation about C7=C8 bond which is evident from the torsion angle (C5—C6—C8—C9= $-177.23(2)^\circ$). The crystal packing is stabilized by C4—H4A...O1 and C13—H13...O1 hydrogen bonds which form inversion dimers (Fig 2 & Table 2). The selected bond lengths and angles are listed in table 3 and 4, respectively.

Table 2: Hydrogen-bond geometry [Å]

D—H...A	Distance (Å)			Angle (°)
	D—H	H...A	D...A	D—H...A
C13—H13...O1 ⁱ	0.93	2.52	3.421 (3)	163
C4—H4A...O1 ⁱⁱ	0.97	2.59	3.458 (3)	150

Symmetry code: i) 1-x,-y,1-z ii) x,1+y,z

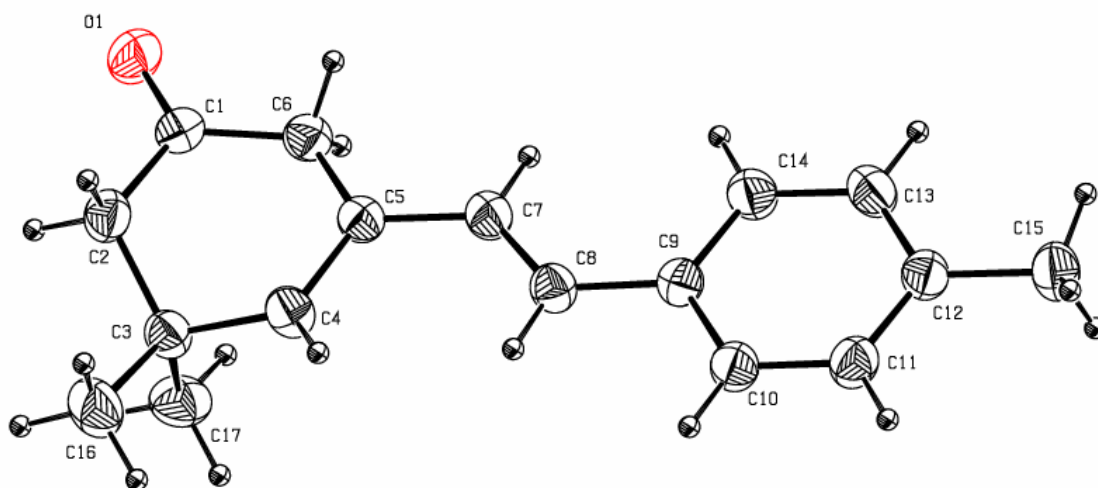


Fig 1. The molecular structure of the titled compound, with atom labeling. Displacement ellipsoids are drawn at the 30% probability level.

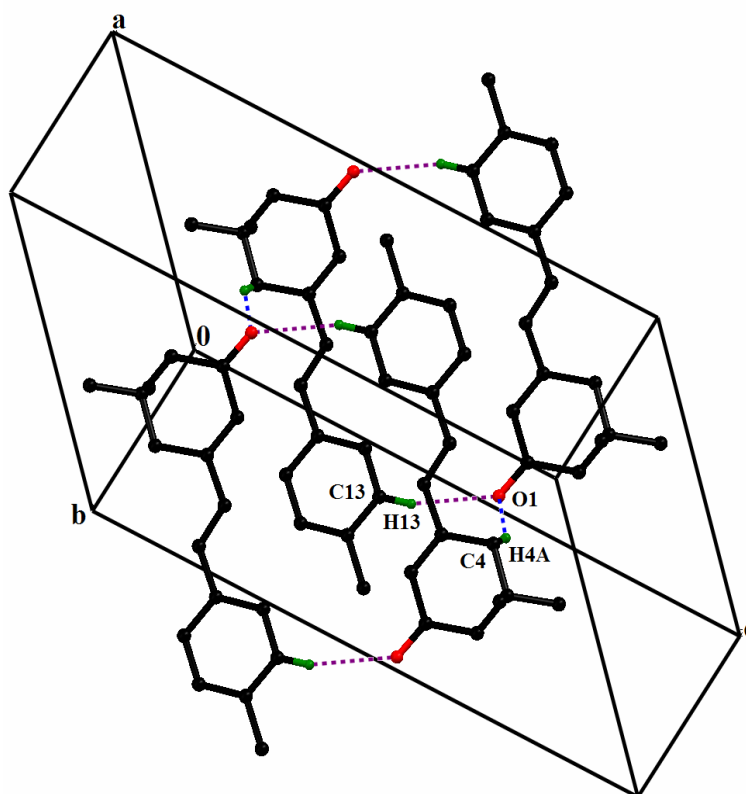


Fig 2. The crystal packing of the titled compound forming inversion dimers viewed down *b* axis. The hydrogen bonds are shown as dashed lines (see Table 2 for details; H-atoms not involved in H-bonds have been excluded for clarity).

Table 3: Selected Bond lengths (Å)

Atom	Length
C(1)-O(1)	1.224(2)
C(1)-C(6)	1.455(2)
C(1)-C(2)	1.493(2)
C(2)-C(3)	1.528(2)
C(3)-C(17)	1.525(2)
C(3)-C(4)	1.528(2)
C(3)-C(16)	1.529(2)
C(4)-C(5)	1.501(2)
C(5)-C(6)	1.347(2)
C(5)-C(7)	1.453(2)
C(7)-C(8)	1.333(2)
C(8)-C(9)	1.463(2)
C(9)-C(14)	1.392(2)
C(9)-C(10)	1.393(2)
C(10)-C(11)	1.383(2)
C(11)-C(12)	1.380(2)
C(12)-C(13)	1.384(2)
C(12)-C(15)	1.507(2)
C(13)-C(14)	1.379(2)

Table 4: Selected Bond angles (°)

Atom	Angle
O(1)-C(1)-C(6)	121.56(1)
O(1)-C(1)-C(2)	121.51(1)
C(6)-C(1)-C(2)	116.91(1)
C(1)-C(2)-C(3)	113.78(1)
C(17)-C(3)-C(2)	109.69(1)
C(17)-C(3)-C(4)	110.03(1)
C(2)-C(3)-C(4)	108.94(1)
C(17)-C(3)-C(16)	109.99(1)
C(2)-C(3)-C(16)	109.32(1)
C(4)-C(3)-C(16)	108.84(1)
C(5)-C(4)-C(3)	114.58(1)
C(6)-C(5)-C(7)	119.81(1)
C(6)-C(5)-C(4)	120.26(1)
C(7)-C(5)-C(4)	119.90(1)
C(5)-C(6)-C(1)	123.42(1)
C(8)-C(7)-C(5)	126.55(1)
C(7)-C(8)-C(9)	127.08(1)
C(14)-C(9)-C(10)	117.03(1)
C(14)-C(9)-C(8)	123.34(1)
C(10)-C(9)-C(8)	119.62(1)
C(11)-C(10)-C(9)	121.22(1)
C(12)-C(11)-C(10)	121.50(1)
C(11)-C(12)-C(13)	117.44(1)
C(11)-C(12)-C(15)	121.44(1)
C(13)-C(12)-C(15)	121.12(1)
C(14)-C(13)-C(12)	121.62(1)
C(13)-C(14)-C(9)	121.18(1)

Conclusion

The crystal structure analysis of a novel cyclohexanone compound was studied using x-ray diffraction method. In the compound, the crystal packing is stabilized by intermolecular C—H...O hydrogen bonds.

Acknowledgments

The authors thank the TBI X-ray facility, CAS in Crystallography and Biophysics, University of Madras, Chennai for data collection. The authors also thank the UGC (SAP-CAS) for the departmental facilities. TS thanks the DST Inspire program for fellowship.

Crystallographic data for the structure reported here have been deposited with CCDC (Deposition No's. CCDC: 1004465). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail: deposit@ccdc.cam.ac.uk.

References

1. Puetz, C., Buschmann, H. & Koegel, B. (2003). US Patent Appl. No.20030096811.
2. Rajveer, C., Stephenrathinaraj, B., Sudharshini, S., Kumaraswamy, D., Bhupendra, S. & Choudhury, P. K. (2010).Res. J. Pharm. Bio. Chem. Sci.1, 99–107.
3. Bruker (2008), APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, US.
4. Sheldrick, G. M. (2008). Acta Cryst. A64, 112–122.
5. Farrugia L. J., J. Appl. Cryst., (1997), 30, 565.
6. Cremer, D. & Pople, J. A. (1975).J. Am. Chem. Soc.97, 1354–1358.
