

# Crystal Structure of 2,6-dibenzylidene cyclodexanone

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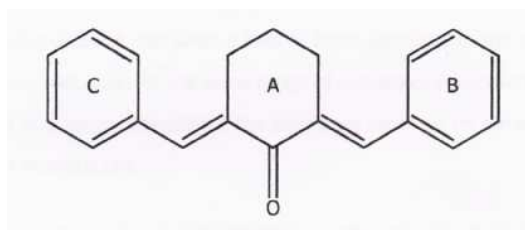
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**Abstract:** The Crystal Structure of 2,6-dibenzylidene cyclodexanone,  $C_{24}H_{32}N_2O_4$ , is synthesized, and its crystal structure is determined by X-ray structure analysis. The crystals are Monoclinic, having space group  $P2_1/c$ ,  $a = 9.589(7) \text{ \AA}$ ,  $b = 18.397(1) \text{ \AA}$ ,  $c = 9.438(7) \text{ \AA}$ ,  $Z = 4$ ,  $R = 0.0694$  for 3250 observed reflections. In crystal, there is an extensive overlap of molecules in the unit cell and there is no intra or intermolecular interaction. However, the structure is stabilized by Van der Waal's forces. The crystal structure was solved by direct method using single crystal X-ray diffraction data collected at room temperature and refined by full-matrix least-squares procedures.

**Keywords:** Cyclodexanone; Crystal structure; Van der Waal's forces; direct method; Diffractometer.

## 1. Introduction

Dibenzylidene derivatives are low-molecular weight organic molecules that can get a variety of organic solvents and polymers by self-assembling into a three-dimensional fibrillar network through weak non-covalent interactions [1]. Dibenzylidene derivatives have been studied in different Polymeric matrices experimentally and revealed to have a crucial role of interactions with bioactive compounds due to their self-assembling organization [2]. 2,6-dibenzylidene cyclohexanone is a cyclic conjugated compound and has been reported to have high cytotoxicity to P388 leukemia cells [3]. Dibenzylidene Sorbitol (DBS) is an organic molecule capable of physical gelation in a wide variety of dental monomers by forming three-dimensional networks [4].



**Figure 1:** 2,6-Dibenzylidene Cyclohexanone

## 2. Experimental

Dissolve NaOH in 25 ml water, add ethanol and cool the mixture. Mix benzaldehyde and cyclohexanone in a 100 ml conical flask followed by addition of alcoholic alkali solution. Stir the mixture for 15 min. at room temperature till precipitates are obtained. Then, filter with suction, wash with cold water and dry on filter paper at room temperature. Recrystallize it from chloroform. A platey shaped single crystal of title compound with the well-defined morphology (dimensions 0.3 x 0.2 x 0.2 mm) was selected for preliminary X-ray photographic studies. The preliminary X-ray

photographic techniques such as Oscillation, Rotation and Weissenberg were employed to ascertain the crystalline nature of any grown compound and this provides a first hand information to a crystallographer to move ahead for the collection of X-ray diffraction data using a BRUKER AXS computer controlled single crystal X-ray diffractometer. The diffractometer provide reflections of various individual planes and their corresponding intensities were recorded electronically with the help of CCD by using MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ).  $\omega$ - $2\theta$  scan mode was employed for the data collection. The Unit Cell Parameter from the X-ray film were calculated by making use of various equations but the values of Unit Cell Parameters as obtained from the diffractometer were used [ $a = 9.589(7) \text{ \AA}$ ,  $b = 18.397(1) \text{ \AA}$ ,  $c = 9.438(7) \text{ \AA}$ ,  $\beta = 95.830(1)$ ]. Since these values were more precise in nature, the cell measurement and refinement was carried at 293 (2) K. A total of 16580 reflections were collected in the  $\theta$ -range  $2.21^\circ$  to  $28.28^\circ$  of which 3518 were found to be unique (with index range;  $-12 \leq h \leq 12$ ,  $-23 \leq k \leq 23$ ,  $-12 \leq l \leq 12$ ). Using the cut off criteria i.e.  $F_0 > 4 \sigma(F_0)$ , 3250 reflections were treated as observed. The reflection data were corrected for Lorentz and Polarization effects.

### 3. Three-dimensional structure analysis:

The structure has been determined by employing Direct methods using SHELXS Software [5]. All non-hydrogen atoms of the molecules were located from the E-map (electron density map). The reliability index for the normalized E-values ( $R_E$ ) comes out to be 0.251. The value of  $\langle |E^2 - 1| \rangle$  is fairly good and is an indicator to know whether the full structure or its principal projections are centric or acentric. The statistical analysis of ABS ( $E^2 - 1$ ) in the SHELXS output indicated overall distribution of intensities to be centric [0.916 (okl); 1.042 (hol); 1.060 (hko)] ( $E$  represents the normalized structure factor).  $R_{\text{int}}$  and  $R_{\text{sigma}}$  values indicated that the intensity data are of good quantity and the values so obtained go very well with the scheme of direct methods.

$$R_{\text{int}} = 0.0245 \text{ and } R_{\text{sigma}} = 0.0189$$

### 4. Structure refinement:

Refinement has been carried out by full-matrix Least squares method on  $F^2$  using SHELXL software [6]. Initially, the isotropic refinement of all the non-hydrogen atoms brought the reliability index down to 0.103 for [ $F_0 > 4F\sigma(F_0)$ ]. The anisotropic refinements with thermal parameters for non-hydrogen atoms converged the R-factor to 0.084. Finally, the R-factor converged to 0.0694 [ $\omega R(F^2) = 0.1453$ ] after few cycles of refinement were employed. The weighing scheme employed is:

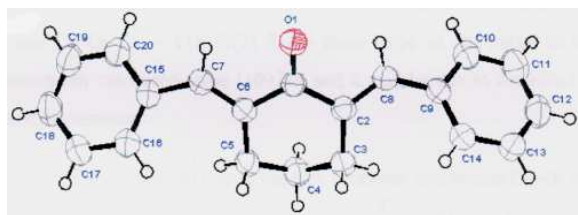
$$\omega = 1/[\sigma^2(F_0)^2 + (0.0416 P)^2 + 0.4967 P]$$

$$\text{where } P = [\text{Max.}(F_0^2, O) + 2Fc^2]/3$$

The goodness-of-fit on  $F^2$  was 1.262. The maximum positive and negative electron density ( $\Delta\rho$ ) in final difference fourier map ranges from 0.193 to  $-0.214 \text{ e. \AA}^{-3}$ , respectively. Atomic scattering factors were taken from International tables for crystallography (1992, vol. C, Tables 4.2.6.8 and 6.1.1.4). Geometrical and other structural calculations were performed by using a PC-Version of PARST [7] Program.

### 5. Results and Discussions

Table 1 contains all the important parameters related to experimental crystal data for the titled compound. A general view of the molecule indicating atomic numbering scheme (thermal ellipsoids drawn at 50% probability' level), is shown in Figure 2 [8]. The geometrical calculations are performed using PARST Program [7].



**Figure 2.** ORTEP view of the molecule.

Molecular geometry of 2,6 dibenzylidene cyclohexanone, more or less, in terms of bond length and bond angles indicate usual values which are comparable with the values reported for some analogous structures in the literature [9-13]. The  $C(\text{Sp}^3) - C(\text{Sp}^3)$  bond length range from 1.498(2) Å–1.522(3) Å with a mean value of 1.508(2) Å for cyclohexanone ring A. The bond distances  $C1-C2 = 1.498(2)$  Å and  $C1-C6 = 1.500(2)$  Å are slightly smaller than the theoretical values, it may be due to the reason that when the electronegativity of oxygen and C-atoms increases causing the decrease in effective atomic radii and then the C–O bond contracts. The  $C(\text{Sp}^2) - C(\text{Sp}^2)$  bond length ranges from 1.336(2) Å – 1.399(3) Å with a mean value of 1.377(3) Å for both the phenyl rings.

The endocyclic bond angles fall in the range of  $110.47(2)^\circ$  to  $119.05(2)^\circ$  [Average value =  $115.33(2)^\circ$ ] for six membered cyclohexanone ring A. The bond angles  $C1-C2-C3 = 117.85(2)^\circ$ ,  $C2-C1-C6 = 119.05(2)^\circ$  and  $C5-C6-C1 = 118.79(2)^\circ$  are quite large as compared to the theoretically calculated value [ $109.20^\circ$ ] and it may be due to the effect of steric hinderances.

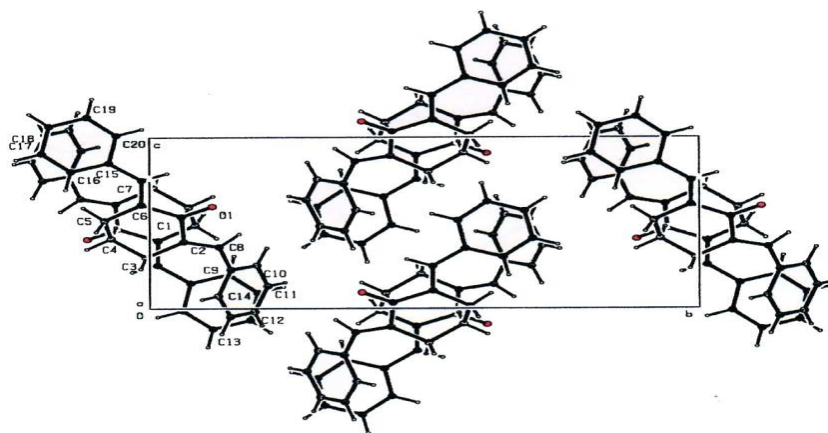
In six-membered ring A, the best rotational axis bisects  $C1-C6$  and  $C3-C4$  bonds with the asymmetry parameter  $\Delta C_2(C1-C6) = 13.15$  [14] and the best mirror plane passes through  $C1$  and  $C4$  with asymmetry parameter  $\Delta C_5(C1-C4) = 8.46$ . The average value of torsion angles in this ring is  $34.8(2)$ . The value of asymmetry parameters and torsion angles make the ring to adopt distorted chair conformation.

The dihedral angle between plane 1, 2 and 3 of the molecule is presented below:

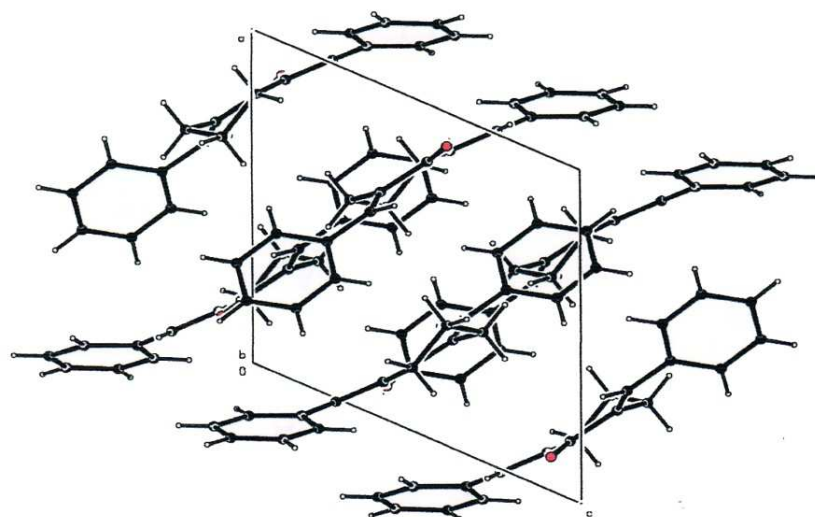
Plane	Plane	Angle ( $^\circ$ )
1	2	58.2 (1)
1	3	37.6 (1)
1	3	38.2 (1)

Ring A and B have dihedral angle of  $58.2^\circ(1)$  whereas it is  $37.9^\circ(1)$  between ring A and C.

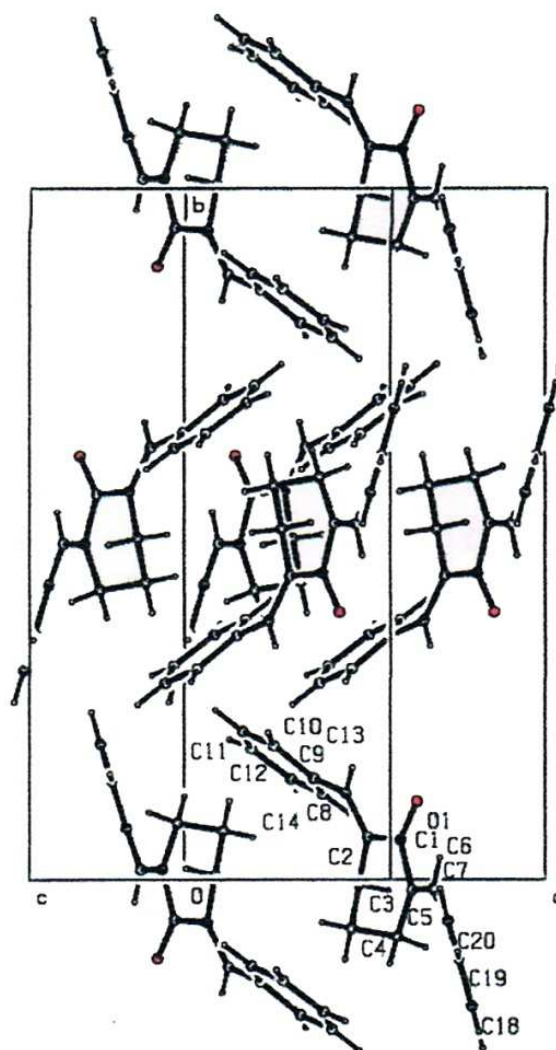
The molecules down a-, b- and c- axis have been plotted in the unit cell are shown in Figure 3, 4 and 5 respectively. There is an extensive overlap of molecules in the unit cell and there is no intra or intermolecular interaction. However, the structure is stabilized by Van der Waal's forces.



**Figure 3:** Unit cell molecular packing down a-axis.



**Figure 4:** Unit cell molecular packing down b-axis.



**Figure 5:** Unit cell molecular packing down c-axis

**Table 1:** Crystal data and structure refinement details

Empirical formula	$C_{24}H_{32}N_2O_4$
Formula weight	412.52
Temperature	293(2)K
Wavelength	0.71073 Å
Crystal size	0.3x0.2x0.2
Unit cell dimensions	a = 9.5890(7) Å, b = 18.3966(14) Å, c = 9.4377(7) Å, $\alpha = \gamma = 90^\circ$ and $\beta = 95.8300(1)^\circ$
Volume	1498.52(19) Å <sup>3</sup>
Crystal system, space group	Monoclinic, P2 <sub>1</sub> /c
Z, calculated density	+, 1.371 Mg/m <sup>3</sup>
Absorption coefficient	0.093mm <sup>-1</sup>
F(000)	666
Theta range for data collection	2.21° to 28.28°
Limiting indices	-12 ≤ h ≤ 12, -23 ≤ k ≤ 23, -12 ≤ l ≤ 12
Reflections collected/unique	16580/3518 [R(int)=0.0245]
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	3518/0/192
Goodness-of-fit on F <sup>2</sup>	1.262
Final R indices [I > 2σ(I)]	R1=0.0694, wR2=0.1453
R indices (all data)	R1=0.0771, wR2=0.1488
Extinction coefficient	0.000(2)
Largest diff. peak and hole	0.193 and -0.214 e.Å <sup>-3</sup>
Software for structure solution	SHELXS86
Software for refinement	SHELXL93
Software for molecular plotting	ORTEP-3
Software for geometrical calculations	PARST

## Conclusions

The title compound, 2,6-dibenzylidene cyclodexanone, has been reported to have high cytotoxicity to P388 leukemia cells by Lakshmi and Ramamurthi, 2005 and this its crystal structure analysis revealed the self-assembling network. The slight deviation in average bond length of cyclohexanone ring from the theoretical value confirms the phenomenon of shortening of bond lengths due to Keto group. The distorted chair conformation of the cyclohexanone ring shows its twisted network. It could be due to the deviation of C4 atom from the mean-molecular axis of ring-A. The ring B and C are inclined at a dihedral angle of 58° and 38° from the cyclohexanone ring. The best packing has been observed down a- and b- axis where the ring B and C look like two rings of a plane (ring A). The packed molecules are progressive diagonally along bc- and ac- plane.

## References

- [1] Marcuccio, S.M. and Elix, J.A., Australian J. of Chemistry. 38(2) (1985) 343-346.
- [2] Frabdrof, W., Fahrlander, M., Fuchs, K. and Friedrich, C, J. of Rheology, Vol. 47(6) (2003) 1445-1454.
- [3] Lakshmi, K. Udaya and Ramamurthi, K.: Cryst. Res. Technol., 40(12) (2005) 1165.
- [4] Joseph, M.A., Elizabeth, A.W., Newell, R.W., Kristen, S.W., Dargo, S., Janet, B.Q., Polymer (2006) in press.
- [5] Sheldrick, G.M. : SHELXL86, Program for Crystal Structure Determination, University of Göttingen, Germany, (1986).
- [6] Sheldrick, G.M. : SHELXL93, Program for Crystal structure Refinement, University of Göttingen, Germany, (1993).
- [7] Nardelli, M. : J. Appl. Cryst. 28 (1995) 659.
- [8] Farrugia, L.J. : Molecular Graphics-ORTEP-3 for windows, L. Appl. Cryst. 30 (1997).
- [9] Yingwu, Jie., Chantrapromma, Suchada., Wenchen., Dong., Peng Tian, Yu., Yung, Ping and Kun Fun, Hoong. : Acta Cryst. C57 (2001) 523.
- [10] Smeets, W.J.J., Spek, A.L. Duisenberg, A.J.M., Labadie, R.P., Desilva, K.T.D., Ratnayake, S.: Acta Cryst. C43 (1987) 1995.
- [11] Gupta, V.K., Rajnikant, Goswami, K.N., Mazumdar, S.K., Gupta, B.D. and Banerjee, S.K. Cryst. Res. Technol, 28(2) (1993) 187.
- [12] Sambyal, V.S., Goswami, K.N. Cryst. Res. Tech
- [13] Fujita, T., Fujitani, R., Takeda, Y., Takaishi, Y., Yamada, T., Kido, M. Miura, I.: Chem. Pharm. Bull., 32 (1984) 2117.vol., 30(5) (1995) 629.
- [14] Duax, W.L., Norton D.A. : Atlas of Steroid Structure, Vol. 1. New York: Plenum (1975).