GROWTH AND CHARACTERIZATION OF
2,6-DIBENZYLIDENECYCLOHEXANONE SINGLE CRYSTAL

4 INTRODUCTION

The unsaturated ketones possess anti-cancer properties [1]. 2,6-dibenzylidenecyclohexanone is a useful precursor for the construction of biologically important heterocycles [2]. Cyclic conjugated bis(benzylidene)ketones have higher cytotoxicity to P388 leukemia cells [3]. In addition, 2,6-dibenzylidenecyclohexanones are discovered as perspective nonlinear optically (NLO) active chromophores in the crystal state and are used in second harmonic generation (SHG) applications [4-8].

4.1 LITERATURE REVIEW

2,6-dibenzylidenecyclohexanone (DBCH) is an organic compound with cyclic conjugated systems. Balaiah and Jeyaraman [9] reported the synthesis of DBCH. This compound has higher cytotoxicity to P388 leukemia cells than the clinically useful drug [3]. A computational study on DBCH was carried out and relative energies of the three possible isomers along with 2,5 - dibenzylidenecyclopentanone (DBCP) were calculated [10]. To consider the effect of the replacement of the central cycloalkanone ring, Jun Kawamata et al. [6] examined the derivatives of DBCH along with DBCP and 2,7 - dibenzylidenecycloheptanone (DBCHEp). A series of p-substituted DBCH equipped with the substituents such as H, CH₃ and CH₃O at the 4-position was found to crystallize in noncentrosymmetric form. They also determined the second harmonic generation intensities by adopting Kurtz and Perry method [11]. The X-ray crystal structure analysis of DBCH
carried out by Zongchao Jia and Quail [2] revealed that this crystal belongs to monoclinic system. Yu et al. [3] reported that bis(benzylidene)cyclo-alkanone exists as nonlinear optically active chromophores and can be used for SHG application. Temperature dependence of absorption spectra and optical parameters for polyester films of dibenzylidenecyclohexanone were reported by Osman et al. [12].

4.2 SIGNIFICANCE OF PRESENT WORK

DBCH has been reported as nonlinear optically (NLO) active chromophores in the crystal state [4-8]. Further, the study of biological activity carried out on DBCH revealed that DBCH has higher cytotoxicity to P388 leukemia cells than the clinically useful drug [3]; thus DBCH has been proved to be an important material for both technological and biological applications. To the best of the knowledge of the author the solubility, growth of DBCH and its characterization have not been reported. Hence, in this chapter the growth of DBCH and some of its characteristics are reported.

4.3 EXPERIMENTAL

A calculated quantity of cyclohexanone, benzaldehyde and absolute ethanol were mixed. This mixture was added to a warm solution of ammonium acetate in absolute ethanol. The mixture was gently warmed on a hot plate till the yellow colour of this solution, formed during the mixing of reactants, just turned into orange. Dry ether was added to the reaction mixture after cooling and the clear solution obtained was kept aside. After a period of three days pale yellow colour crystals of azabicyclic ketone were obtained. These crystals were separated and filtered off. The filtrate, obtained after
isolation of the crude azabicyclic ketone, was concentrated, then
diluted with ether and washed well successively with dilute
hydrochloric acid (3N), sodium bicarbonate (10 %) and water.
Evaporation of the ether from the ethereal layer left behind a resinous
material which after recrystallization from ethanol, gave yellow
crystals of 2,6-dibenzylidene cyclohexanone [9]. The yield was 40 %.
Fig. 4.1 represents the molecular structure of DBCH having the
molecular formula $C_{20}H_{18}O$.

![Molecular Structure of DBCH](image)

**Fig. 4.1 Molecular Structure of DBCH**

### 4.3.1 CHOICE OF SOLVENT

Growth of organic crystals having well developed faces and good
optical quality mainly depends on the selection of suitable solvents.
Solvents offering moderate solubility-temperature gradient for a
material and yielding prismatic growth habit will be considered as
suitable solvents for growing crystal of that material. Another
important factor that influences the habit of growing crystal is the
polarity of the solvents [13-15]. Hence, in this study a few organic
solvents were employed to identify a reasonable solvent. Table. 4.1
presents the electric dipole moments of these solvents [16] and their
influence on the growth habits of DBCH crystal. From this test acetone and ethanol were found to yield prismatic growth. Since the crystals obtained from ethanol were found to be relatively transparent, ethanol was selected as the suitable solvent to grow 2,6-dibenzylidene-cyclohexanone.

Table 4.1 Effect of solvents on the growth habits of DBCH crystal

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Electric dipole moment (Debye)</th>
<th>Morphology</th>
<th>Visual quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0</td>
<td>Platelet</td>
<td>Good</td>
</tr>
<tr>
<td>Acetone</td>
<td>2.88</td>
<td>Prismatic</td>
<td>Good</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.69</td>
<td>Prismatic</td>
<td>Good</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>0</td>
<td>Prismatic</td>
<td>poor</td>
</tr>
</tbody>
</table>

4.3.2 SOLUBILITY AND METASTABLE ZONEWIDTH OF DBCH

The solubility of DBCH in ethanol was determined for different temperatures in the range of 30 – 50° C. The beaker containing 100 ml of the solution was covered tightly and maintained at a constant temperature of 30° C. It was continuously stirred using a magnetic stirrer. The amount of DBCH required to saturate the solution at this temperature was estimated and this process was repeated for different temperatures.

The solubility data obtained in this work was used to measure the metastable zonewidth. These studies were carried out in a
constant temperature bath having an accuracy of ±0.01° C. A constant volume of 100 ml of the solution was used in all these experiments. The solution was superheated 5° C above the saturation temperature and maintained at this temperature for an hour. Metastable zonewidth was measured by conventional polythermal method [17, 18], where the saturated solution is cooled from the experimental temperature to a temperature at which the appearance of first speck of particle is observed. The metastable zonewidth of DBCH solution was estimated under both the stirring and nonstirring conditions of the solutions. The solubility curve along with metastable zonewidth is presented in Fig. 4.2.

4.3.3 GROWTH OF DBCH CRYSTAL

Saturated solution of 100 ml was prepared at 35° C using recrystallized DBCH salt. The solution was filtered with microfilters and taken in a glass beaker of 250 ml capacity. One of the better quality seed crystals of dimension about 0.5x0.3x0.1 mm³ was mounted on a glass stand and placed carefully in the beaker containing saturated solution. Then the beaker was hermetically sealed and placed in a constant temperature bath having an accuracy of ±0.01° C. The growth process was initiated without stirring the solution at 35° C and the temperature was reduced at a rate of 0.2° C per day. After a growth period of six days, well developed and optically transparent DBCH crystal of dimension 22x15x5 mm³ was harvested and is presented in Fig. 4.3.
Fig. 4.2 Solubility curve and metastable zonewidth of DBCH

Fig. 4.3 Harvested DBCH crystal
4.4 STRUCTURAL ANALYSIS

4.4.1 SINGLE CRYSTAL X-RAY DIFFRACTION

Single crystal X-ray diffraction study was carried out using ENRAF NONIUS CAD 4 diffractometer with MoKα radiation (λ = 0.7170 Å) on the as grown DBCH single crystal. The present study shows that DBCH crystallizes in monoclinic system. The unit cell parameters calculated are a = 9.5087 Å, b = 18.5431 Å, c = 9.6523 Å with β = 116°. The schematic diagram of the morphology of the grown crystal along with different crystallographic faces is presented in Fig. 4.4.

![Diagram of DBCH crystal morphology](image)

Fig. 4.4 Morphology of DBCH

4.4.2 FOURIER TRANSFORM INFRARED SPECTRUM

FTIR spectrum of DBCH crystal recorded at room temperature using JASCO - 460 plus FTIR spectrometer is shown in Fig. 4.5. The four absorption bands occurred at about 1607, 1573, 1485 and 1433 cm⁻¹ are caused by C=C skeletal in-plane vibrations and they
stand as the diagnostic of aromatic structure \[19\]. Presence of aromatic compound containing adjacent five hydrogen atoms are confirmed by the vibrational frequencies occurred about 751, 736 and 716 cm\(^{-1}\) \[20, 21\]. Thus, the vibrational frequencies observed in the present study reveal the presence of characteristic functional groups and the skeletal structure of aromatic DBCH.

![Fig. 4.5 FTIR Spectrum of DBCH](image)

4.5 **OPTICAL TRANSMITTANCE SPECTRUM**

The optical transmittance spectrum of DBCH was recorded using Shimadzu model 1601. The spectrum recorded in the range of 300 – 1200 nm is shown in Fig. 4.6. The DBCH crystal is transparent in the range 500 and 1000 nm. The short wavelength cutoff at 420 nm and its transparency in the range of 500 – 1000 nm, illustrate that the crystal has good optical quality \[22\].
4.6 MICROHARDNESS STUDIES

The mechanical strength of the DBCH crystal was measured using a Leitz hardness tester fitted with a diamond indenter attached to Leitz incident light microscope. A smooth, flat surface was selected and subjected to this study. Indentations were made for various loads from 5 g to 50 g. Several trials of indentation were carried out on the prominent (-110) face and the average diagonal length was calculated for an indentation time of 10 seconds. The Vickers hardness number \( H_v \) of the crystal was calculated using the relation \( H_v = 1.8544 \frac{P}{d^2} \) where \( P \) is the applied load in kg and \( d \) is the average diagonal length of impression in mm. Fig. 4.7 shows the variation of Vickers hardness number with load for DBCH [22].
Fig. 4.7 Plot of Hv versus P of DBCH crystal.

CONCLUSION

Solubility and metastable zonewidth of biologically important DBCH were measured. The metastable zonewidth estimated under stirring was found to be reduced relative to the corresponding values of unstirred solution. Well-developed and good optical quality DBCH crystals were grown following temperature reduction method. Single crystal X-ray diffraction study revealed that the crystal belongs to monoclinic system with the cell parameters of $a = 9.508 \, \text{Å}$, $b = 18.543 \, \text{Å}$, $c = 9.652 \, \text{Å}$ and $\beta = 116^\circ$. Vibrational frequencies assigned from FTIR spectral analysis confirmed the presence of the various functional groups of DBCH. The UV-Visible spectrum of DBCH showed that the crystal is transparent in the range of $500 - 1000 \, \text{nm.}$
Vickers hardness values measured on (-110) plane gives its mechanical strength.

REFERENCES: