Chapter 5
BENZIL

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Chapter 5

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5.1 Introduction

Although many organic solids have been studied in terms of their chemical and physical properties only a limited number of them had aroused interest in device applications. Benzil $C_{14}H_{10}O_2$ is a molecular crystal which has been studied due to its interesting optical properties (Jerphagon, 1971). Since it is isomorphous with $\alpha$-quartz, Benzil is named "organic quartz" and shows optical activity much greater than quartz. One peculiar property of benzil is that it gains optical activity in crystalline state only (Natalie, 1927, Chaudhiri and El-Sayed, 1967). Benzil is a pale yellow organic crystal with large optical nonlinearities (Sapriel, 1978). Its high symmetry phase is piezoelectric and phase transition occurs at 84 K (Escherick et al., 1973). It belongs to the class of pyroelectric crystals with a permanent dipole moment (Ary and Alain, 1977; Yoshinara et al., 1982; More et al., 1983).

The crystal structure of benzil, $C_6H_5-\text{CO-CO-C}_6H_5$ was first determined by Becker and Rose (1923) and these results were confirmed by Allen
Fig. 5.1  Benzil
(1927). There are three molecules in the unit cell which has a sixfold general position. The molecules lie with their mid point on the crystallographic two fold axis as shown in Fig. 5.2 (Allen, 1927; Knaggs and Lonsdale, 1939). It crystallises in the trigonal trapezohedral class in the space group P3\_12 or its enantiomorph with lattice constants a=0.815 nm and b=1.346 nm. Lines joining the corresponding atoms in the two halves of the molecule are all perpendicular to the twofold axis which bisects the central carbon-carbon bond as shown in Fig. 5.3 (Lonsdale, 1939; Brown and Sadanaga, 1965). They appear as helical chains around the 3\_1 axis, the chains being closely packed. Each molecule has a twofold symmetry axis perpendicular to C(O)-C(O') bond coinciding with the twofold axis in the unit cell. Molecular packing in the crystal viewed along c-axis is shown in Fig. 5.4.

The peculiar properties possessed by the crystal have stimulated many studies on crystalline benzil, viz, Raman (Claus et al., 1970), IR (Wyncke et al., 1980) and XRD (Terauchi et al. 1982) analysis. Occurrence of optical birefringence near 84 K was investigated by More et al. (1987). Studies on the solvent effect on the intensity of molecular electronic transitions in near UV spectra were done by Kaori and Motohiko (1988). Phase related symmetry effect near a multi beam excitation point was observed in the non-centro symmetric crystal of Benzil (Qunshen and Roberto, 1988). Raman spectrum is of particular interest since Raman lines arising from both intermolecular and intramolecular vibrations are observed (Solin and Ramdas, 1968). Acoustic instability was investigated by Brillouin scattering in both high and low temperature phases (Vacher et al., 1981; Hikaru et al., 1982).
Fig. 5.2  A formal benzil molecule which lies with its mid-point on the crystallographic two fold axis, showing bond lengths (Å) and inter-bond angles (°)
Fig. 5.3  Line joining the atoms in the two halves of the molecules which is perpendicular to the two fold axis
Fig. 5.4 Molecular packing in the crystal viewed along c-axis
A few attempts have been made for growing crystals of high quality from solution (Klapper, 1971, Watanabe and Izumi, 1979) as well as from undercooled melt (Scheffen et al. 1981). Dislocation free crystals were obtained from Czochralski growth (Bley et al., 1978). Benzil crystals were also grown by swelling gel with a solution of Benzil and then adding a non-solvent such as water to the top layer (Margaret et al., 1986). None of these methods produced dislocation free crystals.

Here an effort was made to grow benzil crystals of better quality by several experiments at constant temperature. In addition to solution-gel method of growth, gel-swelling method and solution method of growth were employed. An interesting phenomena of liquid drop formation observed in solution-gel study is also reported here.

5.2 Experimental

The chemicals used in this study were of BDH/AR grade. Sodium metasilicate of gel density 1.05 g/cc was prepared and acidified with glacial acetic acid in the pH range 4.5-7. After the gel was set, 1% solution of benzil in acetone was incorporated on the top of the gel. In another set of experiments, 1% solution of benzil in ethanol was poured on the top of the gel.

In the second set of experiments the gel was mixed with acetone so that the gel acetone ratio is 2:1. After about two weeks when the gel was set, 1% solution of benzil in acetone was gently poured. Within a week a yellow drop of liquid appeared over the solution which grew into bigger size as the level of
top solution decreased. Top solution diffused completely into the gel medium in about two months time, the gel becoming completely opaque and small needles of benzil appearing in the gel. Over this gel, pure acetone was added. Within three weeks pale yellow needle crystals of benzil were seen to grow in the top solution.

In gel swelling method, solution of benzil is incorporated with gel of different pH values (5, 6 and 7). 1% (w/v) solution of benzil in acetone and ethanol were tried. Over the set gel an insoluble solvent (water) was added. Large number of long needle shaped crystals were grown in the gel medium.

Experiments by slow evaporation at constant temperature in various solvents were also carried out. Shallow vessels containing saturated solutions in various solvents such as acetone, ethanol and toluene were prepared and placed in a constant temperature bath ($27^\circ C \pm 1^\circ C$).

### 5.3 Observation and discussion

When acetone solution was added over the pure set gel, a yellow spherical liquid drop formed gradually on the gel surface as in Fig. 5.5(A). Just below the interface, an opaque region was formed which extended towards the gel. Below this region tiny crystals of different morphologies were formed. With benzil solution in ethanol, nucleation started within two days and crystals were grown in the solution (3 x 4 x 15 mm) by three weeks (Fig. 5.5(B)).
FIGURE CAPTIONS

5.5(A) Yellow spherical liquid drop formed on gel surface

5.5(B) Benzil crystals grown in ethanol solution

5.5(C) Long needles of benzil obtained by gel-swelling method

5.5(D) Pale yellow needles of benzil observed on top solution (Acetone)

5.5(E) Single crystal of benzil grown from toluene solution

5.5(F) Single crystal of benzil grown from the top solution (Acetone) kept over the gel
In the second approach when acetone was mixed with gel the yellow drop of liquid was formed on the gel within one week. As the top solution diffused into the gel, needles started appearing inside the gel. Over this gel, when pure acetone was incorporated, pale yellow needles of benzil were observed in the top solution fig. 5.5(D). Best yield was obtained over the gel of pH range (4.5-5.0). In gel swelling method tried with acetone and ethanol, pH value 5, 6 and 7 gave consistent results even with different solvents. Thus, pH has a profound effect on the nucleation of benzil crystals in the gel medium. Long needles obtained (Fig. 5.5(C)) by swelling gel method were thin and poor in quality. Of all solvent tried in solution growth, toluene yielded good quality crystals.

5.4 Characterization

5.4.1 Optical microscopy

Optical micrograph of the liquid drop formed in the benzil solution is seen in Fig. 5.5(A). Benzil crystals grown in the ethanol solution kept over the gel is shown in Fig. 5.5(B). Yellow needles of benzil crystals formed in acetone is given in Fig. 5.5(C). Long needles of benzil crystals grown in the gel medium by gel swelling method is shown in Fig. 5.5(D). Figures 5.5(E) and 5.5(F) show the dislocation free crystals obtained in the top solution of benzil kept over the gel.
5.4.2 Infrared analysis

The IR spectrum of benzil crystals grown in this study is shown in Fig. 5.6. The very intense band at 1760 cm\(^{-1}\) is associated with the stretching vibration of the carbonyl grouping in the benzil. Band at 720 cm\(^{-1}\) is due to the C-H out of plane bending. Bands at 3080 cm\(^{-1}\) and 1400 cm\(^{-1}\) can be attributed to CH stretch and CH in plane bending respectively.

5.4.3 X-ray diffraction analysis

X-ray studies were made by Philips diffractometer with wide angle goniometer PW 1050/70 and a proportional detector PW 1965/60 at a scanning speed 2\(^{\circ}\)/minute and chart speed 4 cm/minute. The diffraction pattern of the crystal was recorded using CuK\(_{\alpha}\) target in the 2\(\theta\) range 5 to 50\(^{\circ}\) (Fig. 5.7). The d-values calculated (0.493, 0.356 and 0.737 nm) are found to be in close agreement with those obtained from ASTM index values (0.498, 0.365 and 0.736 nm).

5.4.4 UV-visible spectroscopy

The UV spectrum shown in figure 5.8, of benzil crystals grown in this study are identical to those found in literature. Remarkable solvent intensification of electronic spectra of benzil was reported earlier (Leonard and Blout, 1950). The absorption maximum at 370 nm is obtained when carbon tetrachloride was used as solvent.
Fig. 5.6  Infrared spectrum of benzil crystal
Fig. 5.7  XRD scan of benzil crystal
Fig. 5.8 UV-visible spectrum of benzil crystal
5.5 Conclusion

Of the series of growth experiments conducted for dislocation free crystals, perfect crystals of limited size were obtained from acetone solution kept over the set gel. Gel swelling method yielded needle shaped crystals of poor quality while bigger crystals were obtained from the ethanol solution kept on top of the gel. Bigger crystals obtained from solution growth method contain dislocations.

Morphological differences of crystals were observed with pure gel and acetone mixed gels. pH of the gel had a profound effect on the nucleation of crystals when gel swelling method was used.

Formation of liquid drops in benzil solution before nucleation of crystals is an interesting phenomena which needs further investigation. To have to a better understanding of the origin and the mechanism of the formation of liquid drop, a detailed study of solution properties of the drop is needed.