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# Synthesis, crystal growth and characterization of 1,5-diphenylpenta-1,4-dien-3-one: An organic crystal

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# ABSTRACT

1,5-Diphenylpenta-1,4-dien-3-one ( dibenzalacetone, DBA) was synthesized by a base-catalyzed aldol condensation reaction between benzaldehyde and acetone. High quality single crystals have been grown by the slow evaporation of ethanol solution and the crystal belongs to monoclinic system with centrosymmetric space group C 2/c. The DBA crystals are transparent in the entire visible region and have a lower optical cutoff at ~440 nm. It is stable up to 119 °C and has a good chemical stability. The high resolution X-ray diffraction curve (DC) indicates that the specimen is free from structural grain boundaries. Molecular packing leads to a centrosymmetric arrangement resulting in zero second harmonic generation (SHG;  $\chi^{(2)}=0$ ) efficiency.

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#### 1. Introduction

Chalcones and their analogs are relatively easily available, not only by isolation from the natural products but also by the methods of classical and combinatorial synthesis. The cytotoxic, anticancer, chemopreventative and mutagenic properties of a number of chalcones have been reviewed [1]. The antibacterial, fungistatic and fungicidal properties of these compounds have also been reviewed [2,3]. Chalcones and their analogs are used as potential therapeutic agents in diseases of the cardiovascular system [4]. Chalcones and their heterocyclic analogs exhibit anti-inflammatory, antitumour [5-7], antibacterial, antifungal [8,9], antitubercular, antiviral, antiprotozal and gastroprotective activities [3]. Chalcones present interesting biological properties, such as cytotoxicity [10], anti-herpes acitivity [11] and antitumour acivity [6] and may be useful for the chemotherapy of leishmaniasis [12], among others. In addition, with appropriate substituents, chalcones are a class of nonlinear optical (NLO) materials [13,14]. Recently, it has been noted that among many organic compounds reported for their second harmonic generation, chalcone derivatives have excellent blue light transmittance and good crystallizability [15,16]. Among the many known organic NLO materials, chalcones exhibit extremely high and fast non linearity [13-15,17,18] and show a preference to crystallize

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as non-centrosymmetric structures [19,20]. Another importance of this type of compound is their high photosensitivity and thermal stability, which are used in developing various crystalline electro-optical devices [11,21]. Literature survey reveals that the growth and the structure of 1,5-diphenylpenta-1,4-dien-3-one crystals were not reported. The crystalline perfection plays an important role in device performance, which depends on the growth technique and conditions [22] and therefore, the crystalline quality of the grown crystals are examined by high-resolution X-ray diffractrometry (HRXRD) studies. The grown crystals are also characterized by XRD, FT-IR, FT-Raman, DRS, thermal analysis and Kurtz powder technique.

# 2. Experimental

#### 2.1. Synthesis and crystal growth

The title compound was synthesized according to the reported method [23] with a yield of  $\sim$ 80%. The product was purified by repeated recrystallization from hot rectified spirit (m.p.119 °C).



DBA single crystals were grown using slow evaporation solution growth technique at room temperature. A saturated solution

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Fig. 1. Photographs of as-grown DBA crystals.

of DBA in ethanol was prepared and the solution was stirred for 3 h at room temperature to obtain a homogeneous solution. A small portion of the mother solution was used to get seed crystals by slow evaporation of the solvent. Tiny crystals were obtained in 3 days. Macroscopic defect-free seed crystals of DBA were harvested after attaining a suitable size. One such seed was introduced into the previously prepared mother solution. A beaker containing DBA solution was tightly covered with a thin polythene sheet to control the evaporation rate of the solvent and kept undisturbed in a dust free environment. The photographs of the as-grown DBA crystals are shown in Fig. 1.

#### 2.2. Characterization studies

The single-crystal structure of DBA was carried out from a selected yellow tablet of approximately  $0.28 \times 0.23 \times 0.18$  mm<sup>3</sup>. Crystal data were collected and integrated using an Oxford Diffraction Xcalibur-S CCD system equipped with graphite monochromated Mo K $\alpha$ ( $\lambda$ =0.71073 Å) radiation at 150 K. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least squares against F2 using SHELXL-97 software [24]. The molecular structure was drawn using ORTEP-3. The powder XRD pattern is recorded by PANalytical X'pert PRO X-ray diffractometer. A multicrystal X-ray diffractometer developed at NPL [25] has been used to record high-resolution diffraction curves (DCs). Fourier transform infrared spectra were recorded using AVATAR 330 FT-IR spectrometer. Fourier transform Raman spectra were recorded using FT-RAMAN BRUKER RFS 100/S Instrument. UV-vis spectra were recorded using CARY 5E UV-vis spectrophotometer. DSC curves were recorded on a SDT Q600 (TA instrument) thermal analyzer. DSC analysis of DBA crystal is carried out between 50 and 300 °C in the nitrogen atmosphere. The SHG test on the crystal was performed by the Kurtz powder method [26]. An Nd:YAG laser with modulated radiation of 1064 nm was used as the optical source and directed on the powdered sample through a filter.

# 3. Results and discussion

# 3.1. FT-IR and FT-Raman

In order to confirm the functional groups present in the DBA molecule, FT-IR spectrum was recorded (Fig. 2) in the spectral range of 400–4000 cm<sup>-1</sup>. The absorption bands corresponding to asymmetric and symmetric C–H stretching vibrations of –CH group were observed at 3025 and 3052 cm<sup>-1</sup>, respectively. The weak absorption at summation bands in the range of 2000–1650 cm<sup>-1</sup> were attributed to the aromatic C–H out-of-plane bending. The weak absorption band at 1650 cm<sup>-1</sup> corresponds to the C=O stretching vibration. The relatively stronger absorption band at 1592 cm<sup>-1</sup> and a weaker absorption band at 1493 cm<sup>-1</sup> were due





Fig. 3. FT-Raman spectrum of DBA crystal.

 Table 1

 Observed vibrational bands of DBA in (cm<sup>-1</sup>).

|  |   | FT-IR   | FT-Raman  |
|--|---|---|---|
| Conjugated -C=C-         1625         1626           -C=O stretching         1650         1651           Aromatic vibration and C=C bending<br>modes of $\alpha$ , β-unsaturated carbon         1592 and 1493         1596 and 1449           C-H out-of-plane         1650-2000         1650-2000         1650-2000           C-H stretching of CH=CH         3025 and 3052         3026 and 3060 | Conjugated $-C=C-$<br>-C=O stretching<br>Aromatic vibration and C=C bending<br>modes of $\alpha$ , $\beta$ -unsaturated carbon<br>C-H out-of-plane<br>C-H stretching of CH=CH | 1625<br>1650<br>1592 and 1493<br>1650-2000<br>3025 and 3052 | 1626<br>1651<br>1596 and 1449<br>1650–2000<br>3026 and 3060 |

to aromatic ring vibrations and C=C bending modes of  $\alpha$ ,  $\beta$ -unsaturated carbons, respectively. The absorption bands observed in the region of 1000–800 cm<sup>-1</sup> were the characteristic of C-H outof-plane bending or wagging vibrations of hydrogen atoms attached to unsaturated carbons (alkene). The observed FT-IR and FT-Raman (Fig. 3) vibrational bands of DBA are listed in Table 1.

# 3.2. Powder XRD analysis

The DBA powder sample was scanned in the  $2\theta$  range of  $\sim 2$  (0 is not supposed to be correct)  $-80^{\circ}$  at a scanning rate of  $1^{\circ}/$  min. The results of powder XRD pattern were shown in Fig. 4. The XRD profiles show that all samples were of single phase without detectable impurity. Narrow peaks indicate the good crystallinity of the material, which is further confirmed by HRXRD.

#### 3.3. Diffuse reflectance spectra

UV cutoff is ~440 nm and the absorbance is minimum in the 450–800 nm range (Fig. 5). Comparison of the cutoff  $\lambda$  of DBA



**Fig. 4.** Powder XRD patterns of DBA crystal (a) single crystal structure pattern (b) experimental pattern.



Fig. 5. Diffuse reflectance spectrum of DBA crystal.

#### Table 2

UV data of DBA and substituted DBA in (nm).

| Name of chalcones   | $\lambda \max(nm)$  |
|---|---|
| 1,5-diphenylpenta-1,4-dien-3-one<br>1,5-bis(4-chlorophenyl)penta-1,4-dien-3-one (CDBA) <sup>a</sup><br>1,5-bis(methoxyphenyl)penta-1,4-dien-3-one (PDBA) <sup>b</sup> | $\begin{array}{c} \sim 440 \\ \sim 440 \\ \sim 440 \end{array}$ |

<sup>a</sup> ref [19].

<sup>b</sup> ref **[20]**.

with that of *p*-chlorodibenzalacetone (CDBA) [19] or *p*-methoxy dibenzalacetone (PDBA) [20] shows no significant changes (Table 2) due to *p*-chloro or *p*-methoxy substituents.

## 3.4. Thermal analysis (differential scanning calorimetry)

The DSC was performed to know the thermal behavior of the grown crystals. The DSC of the grown DBA crystal is shown in

#### 3.5. HRXRD

Fig. 7 shows the high-resolution rocking/diffraction curve (DC) recorded for a typical DBA crystal using (010) diffracting planes in symmetrical Bragg geometry by employing the multicrystal X-ray diffractometer with  $MoK\alpha_1$  radiation. As seen in the figure, the DC contains a single peak and indicates that the specimen is free from structural grain boundaries. The FWHM (full width at half maximum) of the curve is 70 arc s, which is somewhat more than that expected from the plane wave theory of dynamical X-ray diffraction [27] for an ideally perfect crystal but close to that expected for nearly perfect real life crystals. This much broadness with good scattered intensity along both the wings of the DC indicates that the crystal contains both vacancy and interstitial type of defects [28]. More details about the size and shape of the defects may be obtained from the study of highresolution diffuse X-ray scattering measurements [25], which is not the main focus of the present investigation. However, such microscopic defects may not have much effect on the device performance, which are many times unavoidable due to thermodynamical considerations and also due to impurities originated



Fig. 6. DSC of DBA crystal.



Fig. 7. HRXRD recorded for DBA crystal.

right from the raw material and/or due to the entrapment of vacancies and solvent molecules [29].

# 3.6. Single crystal XRD

Using single crystal XRD studies, the lattice parameters of DBA are determined and the crystal data are given in Table 3 along with those of CDBA and PDBA. The ORTEP and packing diagrams are shown in Figs. 8 and 9. The DBA molecule is nonplanar. Taking C4–C9 phenyl ring as plane 1 (PL1), C4'–C9' phenyl ring as plane 2 (PL2) and the central C4–C3A=C2A–C1 as plane 3 (PL3), the dihedral angles between them,  $A_{12}$ ,  $A_{13}$  and  $A_{23}$  are 54.85°, 19.9° and 38.26°, respectively, showing that the two phenyl rings are rotated in the opposite directions with respect to the central part, plane 3. The C4–C3A=C2A–C1 torsional angle is 179.2 (6)°.

# 3.7. NLO studies

Chalcones are attractive because their properties can be easily controlled by suitable substitution in the phenyl ring. Substituting different donor and acceptor groups on phenyl rings brings remarkable changes in their physical properties. The *p*-chloro and *p*-methoxy substituted DBA crystals crystallize in a non-centrosymmetric space group leading to high SHG efficiency [19,20]. Being

#### Table 3

Crystal data of DBA and substituted DBA.

centrosymmetric, SHG and second order NLO responses are not exhibited for DBA. But no crystal symmetry restrictions are there for third order NLO responses. The optical switches and optical limiting devices demand materials with fast and large third order optical nonlinearity. Even though SHG is zero in DBA, it is expected to have practical third order NLO applications. In 3-(4-methylphenyl)-1-(3-thienyl)-2-propen-1-one(MTC) [30], the main contribution to SHG results from the strong hydrogen bonds, which appear as intense IR bands of hydrogen bond vibration. No such strong hydrogen bonds are observed in DBA using mercury software and it could be the reason for zero SHG. Wu et al. [31] suggested from their theoretical hyperpolarizability studies on 1.5-diphenylpenta-2.4-dien-1-one molecules that the carbonyl group present at the middle splits of the conjugated system into two relatively independent bonds. Chalcones are regarded as cross conjugated molecule that possesses two independent hyperpolar parts to have a 2D  $\beta$  characters. Large SHG is due to unidirectional



Fig. 9. Packing diagram of DBA crystal.

|                            | 1,5-diphenylpenta-1,<br>4-dien-3-one    | 1,5-bis(4-chlorophenyl)<br>penta-1,4-dien-3-one <sup>a</sup> | 1,5-bis(4-methoxyphenyl)<br>penta-1,4-dien-3-one <sup>b</sup> |
|----------------------------|---|--|---|
| Molecular formula          | C <sub>17</sub> H <sub>14</sub> O       | C <sub>17</sub> H <sub>12</sub> Cl <sub>2</sub> O            | C <sub>19</sub> H <sub>18</sub> O <sub>3</sub>                |
| Molecular weight (gm/mole) | 234.28                                  | 303.17   | 294.33  |
| Melting point (°C)         | 116                                     | 193  | 131   |
| Color                      | Pale yellow                             | colorless  | Pale yellow   |
| Space group                | Monoclinic,C2/c                         | Orthorhombic, P21 21 2                                       | Orthorhombic,Aba2   |
| Unit cell dimensions       | a=28.4700(19) Å                         | a=24.509(3) Å  | a=33.5830(6) Å  |
|                            | b=5.8108(3) Å                           | b=4.9846(5) Å  | b=7.2756(9) Å   |
|                            | c=7.7929(5) Å                           | c=5.8103(6) Å  | c = 6.132(5)  Å   |
|                            | $\beta = 100.163(6)^{\circ}$            | $\beta = 90^{\circ}$   | $\beta = 90^{\circ}$  |
| Volume                     | 1268.98(13) Å <sup>3</sup>              | 709.82 (13) Å <sup>3</sup>                                   | 1498.3 (12) Å <sup>3</sup>                                    |
| Z                          | 8                                       | 2  | 4   |
| Crystal size               | $0.28~mm \times 0.23~mm \times 0.18~mm$ | $0.38~mm \times 0.36~mm \times 0.28~mm$                      | $0.52~mm \times 0.22~mm \times 0.04~mm$                       |

<sup>a</sup> ref **[19]**.

<sup>b</sup> ref **[20]**.



Fig. 8. ORTEP diagram of DBA crystal.

arrangement of molecular dipoles in which  $\mu$  of each molecule adds to establish a net polarization. To maximize  $(\chi^{(2)})$  it is necessary to have a head-to-tail alignment of molecules connected through strong intermolecular hydrogen bond interactions. The zero SHG in DBA could be due to anti-parallel alignment of molecular dipoles, in which the u of each molecule gets canceled. Classic hydrogen bonds are not observed in the present study except for some weak  $\pi$  interactions.

# 4. Conclusions

1,5-Diphenylpenta-1,4-dien-3-one (DBA) crystals were grown in ethanol and the structure was solved by single crystal X-ray analysis. Interestingly, the unsubstitued DBA crystallizes in a centrosymmetry space group in contrast to the noncentrosymmetry exhibited by para-substituted DBA crystals. The specimen is free from structural grain boundaries as observed by HRXRD studies. We have also used XRD, FT-IR, FT-Raman, DRS, thermal analysis and Kurtz powder technique to characterize the grown organic crystal.

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