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# Synthesis, structure, growth and characterization of an organic crystal: 1,5-diphenylpenta-2,4-dien-1-one

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1,5-Diphenylpenta-2,4-dien-1-one (DDO) chalcone single crystals, synthesized by a base-catalysed aldol condensation reaction between cinnamaldehyde and acetophenone, have been grown by the slow evaporation of an ethanol solution. The crystals belong to the orthorhombic system with centrosymmetric space group Pbca. The DDO crystals are transparent in the visible region and have a lower optical cut-off at  $\sim$ 445 nm with a band-gap energy of 2.87 eV. Thermogravimetry/differential scanning calorimetry thermal analysis shows that the crystal is stable up to 375 K and it has a good chemical stability. The vibrational patterns of the chalcone have been investigated by Fourier transform IR and Fourier transform Raman spectroscopy. Microhardness studies were also carried out to elucidate the mechanical behaviour. Theoretical calculations were performed using the Hartree–Fock method with 6-31G(d,p) as the basis set, and the first-order hyperpolarizability is  $7.077 \times 10^{-30}$  electrostatic units, which is >25 times that of urea. The crystalline perfection evaluated by high-resolution X-ray diffraction analysis reveals multiple peaks. The molecular packing leads to a centrosymmetric arrangement, resulting in zero second harmonic generation  $[\chi^{(2)} = 0]$  efficiency. Interestingly, the bromo- and chloro-substituted chalcones are good nonlinear optical materials.

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# 1. Introduction

Chalcones and their analogues are relatively easily available, not only by isolation from 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 (Dimmock et al., 1999). The antibacterial, fungistatic and fungicidal properties of these compounds have also been reviewed (Opletalova, 2000; Opletalova & Sedivy, 1999). With appropriate substituents, chalcones are a class of nonlinear optical (NLO) materials (Fichou et al., 1988; Goto et al., 1991). 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 (Bertl et al., 2004; Kitaoka et al., 1990). Among the many known organic NLO materials, chalcones exhibit extremely high and fast nonlinearity (Fichou et al., 1988; Goto et al., 1991; Bertl et al., 2004; Uchida et al., 1998; Zhang et al., 1990) and show a preference to crystallize as noncentrosymmetric structures (Ravindra, Kiran, Dharmaprakash et al., 2008; Ravindra, Kiran, Nooji et al., 2008). Another importance of this type of compound is its high photosensitivity and thermal stability, which are used in developing various crystalline electro-optical devices (Williams, 1983). The first-, second- and third-order polarizabilities of 26 derivatives of 1,5-diphenylpenta-2,4-dien-1-ones (DDOs) and 18 chalcones were systematically calculated and studied with the *ab initio* molecular orbital method. It was revealed that the DDO molecules had high hyperpolarizabilities; the intramolecular charge transfer from the diene portion to the carbonyl group is the dominating contributor to the molecular charge transfer, and in turn the main influencing factor of hyperpolarizabilities (Wu et al., 2004). A literature survey reveals that the growth aspect of 1.5-diphenylpenta-2,4-dien-1-one crystals has not been reported. We have therefore undertaken the current study of DDO. The crystalline perfection plays an important role in device performance, which depends on the growth technique and conditions (Vijayan et al., 2006). Therefore, the crystalline quality of the grown crystals has been examined by high-resolution X-ray diffraction (HRXRD) studies. The grown crystals are also characterized by X-ray diffraction (XRD), Fourier transform (FT) IR, FT-Raman, UV-Vis, thermal analysis, microhardness studies and the Kurtz powder technique.

# 2. Experimental

# 2.1. Synthesis and crystal growth

The title compound was synthesized using cinnamaldehyde (Loba Chemie) and acetophenone (E-Merck) according to the

previously reported method (Furnis *et al.*, 1989) with a yield of  $\sim$ 80%. Acetophenone (0.01 mol) was mixed with cinnamaldehyde (0.01 mol) in ethanol and the mixture was treated with 10% sodium hydroxide. The mixture was stirred well and put aside for 24 h, and DDO was obtained as a yellow precipitate. The resulting yellow solid mass was collected by filtration and dried. The synthesized material was further purified by repeated recrystallization from hot rectified spirit (m.p. 375 K). The chloro- and bromo-substituted chalcones were synthesized by aldol condensation using substituted acetophenone and cinnamaldehyde.



DDO single crystals were grown using the slow evaporation solution growth technique at room temperature. Many organic solvents such as ethanol, methanol, acetone and acetonitrile were tried as a medium, and ethanol was found to be suitable for the growth of perfect crystals. A saturated solution of DDO in ethanol was prepared and the solution was stirred for 3 h at room temperature to obtain a homogeneous solution. A beaker containing DDO 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. Tiny crystals were obtained in a period of 4–5 d. Defect-free seed crystals of DDO were used for bulk growth. Photographs of the as-grown DDO crystals are shown in Fig. 1.

# 2.2. Characterization studies

The structural analysis of DDO was carried out for a selected yellow tablet of approximately  $0.20 \times 0.20 \times 0.30$  mm using a Bruker Kappa APEXII X-ray diffractometer. Singlecrystal XRD data were collected on a diffraction system that employs graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda$  = 0.71073 Å). The structures were solved and refined by fullmatrix least squares on  $F^2$  with the WinGX software package (Farrugia, 2012), utilizing the SHELXS97 and SHELXL97 (Sheldrick, 2008) modules.<sup>1</sup> The plots for the structures were created with the DIAMOND software (Brandenburg, 2007). All non-H atoms were refined anisotropically. The powder XRD pattern was recorded by a PANalytical X'pert PRO X-ray diffractometer. FT-IR spectra were recorded using an AVATAR 330 FT-IR spectrometer. FT-Raman spectra were recorded using a Bruker RFS 100/S instrument. A CARY 5E UV-Vis spectrophotometer was used for the UV-Vis studies. Thermogravimetry/differential scanning calorimetry (TG/ DSC) curves were recorded on an SDT Q600 (TA Instruments) thermal analyser. The Vickers microhardness was evaluated for the well polished grown crystal using a Reichert 4000E ultramicrohardness tester.

To evaluate the crystalline perfection of the specimen crystals, HRXRD analysis was carried out. A multicrystal X-ray diffractometer developed at the National Physical Laboratory, New Delhi (Lal & Bhagavannarayana, 1989), was used to record high-resolution rocking or diffraction curves (DCs). In this system, a fine focus  $(0.4 \times 8 \text{ mm}; 2 \text{ kW Mo})$ X-ray source energized by a well stabilized Philips X-ray generator (PW 1743) was employed. A well collimated and monochromated Mo  $K\alpha_1$  beam obtained from the three Si monochromator crystals set in a dispersive (+, -, -) configuration was used as the exploring X-ray beam. The diffracted intensity was measured by using a scintillation counter. The DCs were recorded by changing the glancing angle (the angle between the incident X-ray beam and the surface of the specimen) around the Bragg diffraction peak position  $\theta_{\rm B}$ (taken as zero as a reference point) starting from a suitable arbitrary glancing angle  $(\theta)$ . The detector was kept at the same angular position  $2\theta_{\rm B}$  with a wide opening for its slit, the socalled  $\omega$  scan (Bhagavannarayana & Kushwaha, 2010). Before recording the diffraction curve, to remove the noncrystallized solute atoms remaining on the surface of the crystal and also to ensure the surface planarity, the specimens were first lapped and chemically etched in a nonpreferential etchant of water and acetone mixed in a 1:2 volume ratio.

A Hartree–Fock calculation was performed using the *GAUSSIAN03* (Frisch *et al.*, 2004) program package on a personal computer without any constraints on the geometry, using 6-31G(d,p) as the basis set (Schlegel, 1982). By the use of the *GAUSSVIEW* molecular visualization program (Frisch *et al.*, 2000) the optimized structure of the molecule has been visualized. The second harmonic generation (SHG) test on the crystal was performed by the Kurtz powder method (Kurtz & Perry, 1968). An Nd:YAG laser, providing modulated radiation of 1064 nm with an input radiation of 2.35 mJ per pulse, was used as the optical source and directed onto 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 DDO molecule, an FT-IR spectrum was recorded (Fig. 2a) in



Figure 1 Photographs of as-grown DDO crystals.

<sup>&</sup>lt;sup>1</sup> Supplementary data for this paper are available from the IUCr electronic archives (Reference: RG5013). Services for accessing these data are described at the back of the journal.

#### Table 1

Observed vibrational bands of DDO crystals (cm<sup>-1</sup>).

|   | FT–IR         | FT–Raman      |
|---|---------------|---------------|
| -C=O stretching                             | 1654          | 1654          |
| Aromatic vibration and C=C bending          | 1586 and 1445 | 1585 and 1452 |
| modes of $\alpha,\beta$ -unsaturated carbon |               |               |
| C-H out of plane                            | 1650-2000     | 1650-2000     |
| C-H stretching of CH=CH                     | 3022 and 3063 | 3061          |

the spectral range of  $400-4000 \text{ cm}^{-1}$ . The absorption bands corresponding to asymmetric and symmetric C-H stretching vibrations of the -CH group were observed at 3022 and 3063 cm<sup>-1</sup>, respectively. The weak absorption features at summation bands in the range of  $2000-1650 \text{ cm}^{-1}$  were attributed to the aromatic C-H out-of-plane bending. The weak absorption band at 1654  $\text{cm}^{-1}$  corresponds to the C=O stretching vibration. The relatively stronger absorption band at 1586  $\text{cm}^{-1}$  and a weaker absorption band at 1445  $\text{cm}^{-1}$  are due to aromatic ring vibrations and C=C bending modes of  $\alpha,\beta$ -unsaturated C atoms, respectively. The absorption bands observed in the region of 1000-800 cm<sup>-1</sup> are characteristic of C-H out-of-plane bending or wagging vibrations of H atoms attached to unsaturated C atoms (alkene). The observed FT-IR and FT-Raman (Fig. 2b) vibrational bands of DDO are listed in Table 1.

#### 3.2. Powder XRD analysis

The powder XRD pattern is shown in Fig. 3. The XRD profiles show that all samples were of single phase without detectable impurity. The well defined Bragg peaks at specific  $2\theta$  angles show the high crystallinity of the DDO crystal. The crystallite size (*t*) of the DDO crystal is calculated (59 nm) using the Scherrer equation:



Vibrational patterns: (a) FT–IR and (b) FT–Raman.

# $t = k\lambda/\beta\cos\theta,\tag{1}$

where k is the Scherrer constant,  $\lambda$  is the X-ray wavelength,  $\theta$  is the peak position measured in radians and  $\beta$  is the integral breadth of reflections (in radians  $2\theta$ ) located at  $2\theta$ .

# 3.3. Optical studies

The optical absorption spectrum of the DDO crystal is shown in Fig. 4. The crystal has good transmission in the entire visible region and the lower cut-off wavelength is ~445 nm. The measurement of the absorption coefficient  $\alpha$  as a function of frequency  $\nu$  of the incident beam provides a means to determine the band gap  $E_g$  of a material. The optical absorption coefficient ( $\alpha$ ) was calculated using the relation

$$\alpha = (2.303/d) \log(1/T), \tag{2}$$

where T is the transmittance and d is the thickness of the crystal. The optical band gap in most materials can be determined using the Tauc relation, which is expressed as

$$(\alpha h\nu) = A(h\nu - E_g)^r, \qquad (3)$$



Powder XRD pattern of a DDO crystal.



**Figure 4** UV–Vis spectrum (the Tauc plot is given as an inset).

where A is a constant, h is Planck's constant and r is an index that depends on the nature of electronic transition responsible for the optical absorption. The Tauc plot of the optical absorption spectrum measured at room temperature for DDO is given as an inset in Fig. 4. The direct optical energy gap can be obtained from the intercept of the resulting straight lines with the energy axis at  $(\alpha h v)^2 = 0$ , and the band-gap energy of the specimen is deduced as 2.87 eV with an absorption edge at 432 nm (Fig. 4).

#### 3.4. Thermal analysis

TG/DSC was performed to investigate the thermal behaviour of the as-grown crystals (Fig. 5). In the DSC analysis, a sharp endothermic peak was found at around 376 K, and it was assigned to the melting point, at which no weight loss has been noticed in the TG analysis. Below this endotherm, no exothermic or endothermic peak is observed. In the thermogravimetric analysis, the material exhibits single-stage weight loss starting around 543 K, which may be due to the decomposition of the DDO, and below this temperature no significant weight loss is observed. The sharpness of the endothermic peak observed with DSC shows the good degree of crystallinity of the material. No decomposition up to the melting point ensures the stability of the material for laser applications where the crystals are required to withstand high temperatures. The sharp endotherm is indicative of a solid-state transition for relatively pure material. The melting point was also determined by using a Sigma Instruments melting point apparatus (372–373 K).

#### 3.5. Mechanical studies

Transparent crystals free from cracks were selected for microhardness measurements. Before indentation, the crystals were carefully lapped and washed to avoid surface defects. Vickers hardness indentations were made on the as-grown surface of the DDO crystals at room temperature with a load ranging from 25 to 100 g, keeping the time of indentation as 10 s for all trials. The Vickers hardness number,  $H_v$ , was calculated from the following equation:





TG/DSC of a DDO crystal.

where P is the applied load in kilograms and d is the mean diagonal length of the indentation impression in micrometres. As seen in Fig. 6, the hardness of the grown crystal increases as the load increases. Cracks started developing around the indentation mark beyond a load of 100 g. This may be a result of the internal stresses released during the indentation. The work hardening index is equal to 4.4.

#### 3.6. HRXRD

Fig. 7 shows the high-resolution X-ray diffraction curve recorded using Mo  $K\alpha_1$  radiation for a typical DDO singlecrystal specimen. On careful observation, the curve does not seem to be a single peak. The solid line (convoluted curve) is well fitted with the experimental points represented by the filled circles. On deconvolution of the diffraction curve, it is clear that the curve contains an additional peak, which is 125" away from the higher-intensity peak. The additional peak corresponds to an internal structural low-angle boundary. For a better understanding, a schematic of a structural grain boundary is given in the inset of Fig. 7. As seen in the inset,



A plot of Vickers hardness number (kg mm<sup>-2</sup>) versus load (g).



HRXRD of a DDO crystal.

two regions of the crystal are misoriented by a finite angle  $\alpha$ , also known as the tilt angle. The tilt angle may be defined as the misorientation angle between the two crystalline regions on opposing sides of the structural grain boundary. The two regions may be perfect. If  $\alpha \leq 1'$ , we may call it a very low angle boundary. If  $1' < \alpha < 1^\circ$ , we call it a low-angle boundary. More details of such structural grain boundaries, including their affect on physical properties, are available elsewhere (Bhagavannarayana et al., 2005; Bhagavannarayana & Kushwaha, 2010). The angular separation between the two peaks gives the tilt angle  $\alpha$ , which is 125" for the specimen crystal as seen in the figure. The FWHMs of the main peak and the lowangle boundary are, respectively, 120 and 220". These relatively high values reveal the fact that both the regions of the crystal are not perfect. These types of structural defects are probably generated in the crystals as a result of mechanical/ thermal fluctuations that occurred during the growth process and/or because of the fast growth (Bhagavannarayana et al., 2010). It may be mentioned here that such minute defects could be detected with well resolved peaks in the diffraction curve only because of the high resolution of the diffractometer. The influence of such defects may not reflect much on the NLO properties. However, a quantitative analysis of such unavoidable defects is of great importance, particularly in the case of phase matching applications as explained in our recent article (Bhagavannarayana et al., 2011).

# 3.7. Single-crystal XRD

The structural analysis of the DDO crystal was carried out by single-crystal XRD analysis. The displacement ellipsoid plot of DDO is given in Fig. 8(a). The compound crystallizes in



#### Figure 8

(a) Displacement ellipsoid plot of the title compound. (b) Optimized molecular structure.

| Chalcone  | $I_{2\omega}$ (mV)                             |
|---|--|
| 1,5-Diphenylpenta-2,4-dien-1-one  | 0  |
| 1-(4-Bromophenyl)-5-phenylpenta-2,4-dien-1-one  | 2 times that of KDP                            |
| 1-(4-Chlorophenyl)-5-phenylpenta-2,4-dien-1-one   | 5 times that of KDP                            |
| 1,5-Diphenylpenta-1,4-dien-3-one <sup>a</sup>   | 0  |
| 1,5-Bis(4-chlorophenyl)penta-1,4-dien-3-one <sup>b</sup><br>1,5-Bis(4-methoxyphenyl)penta-1,4-dien-3-one <sup>c</sup> | 4.5 times that of urea 15.5 times that of urea |

References: (a) Vanchinathan et al. (2011); (b) Ravindra, Kiran, Dharmaprakash et al. (2008); (c) Ravindra, Kiran, Nooji et al. (2008).

the orthorhombic crystal system with centrosymmetric space group Pbca, and the obtained cell parameter values,  $a = 15.4307 (9), \quad b = 10.2659 (5), \quad c = 16.4124 (9) \text{ Å}, \quad V = 10.2659 (5), \quad c = 10.2659$ 2599.9 (2)  $Å^3$  and Z = 8, are in good agreement with the reported values (Kashino & Haisa, 1980). The DDO molecule is planar. Taking the C1-C6 phenyl ring as plane 1, the C12-C17 phenyl ring as plane 2 and the central C7-C11 linkage as plane 3, the dihedral angles between them,  $A_{12}$ ,  $A_{13}$  and  $A_{23}$ are 0.69, 19.91 and 19.53°, respectively, showing that the two phenyl rings are rotated in opposite directions with respect to the central plane 3. The C6-C7-C8-C9 and C9-C10-C11-C12 torsion angles are -160.63(18) and  $178.39(18)^{\circ}$ . respectively. The internal angle at the ring atom (C6) to which the carbonyl C atom (C7) is bonded is  $118.4^{\circ}$ , while the internal angle at the equivalent atom (C12) in the other ring is slightly smaller (117.36°).

# 3.8. NLO studies

Chalcone properties can be easily controlled by suitable substitution in the phenyl ring. Substituting different donor and acceptor groups on phenyl rings can result in remarkable changes in the physical properties. Being centrosymmetric, DDO crystals do not exhibit SHG when they are exposed to an Nd:YAG laser (1064 nm), but there are no crystal symmetry restrictions for third-order NLO responses. Interestingly, even though SHG is zero in DDO, the p-bromo- and p-chloro-substituted DDO crystals exhibit a considerable SHG efficiency and the performance of 1-(4-chlorophenyl)-5phenylpenta-2,4-dien-1-one is striking (Table 2). Interestingly, in the related 1,5-diphenylpenta-1,4-dien-3-one crystals (Vanchinathan et al., 2011), high efficiency is also exhibited by the p-chloro (Ravindra, Kiran, Dharmaprakash et al., 2008) and p-methoxy (Ravindra, Kiran, Nooji et al., 2008) derivatives. NLO behaviour depends on structure and orientation. A favourable molecular alignment in the case of substituted chalcones leads to high SHG efficiency,  $\chi^{(2)}$ . To maximize  $\chi^{(2)}$ it is necessary to have a head-to-tail alignment of molecules connected through strong intermolecular hydrogen-bond interactions. The absence of SHG in DDO could be due to antiparallel alignment of molecular dipoles, in which the dipole moment,  $\mu$ , of each molecule gets cancelled. Classic hydrogen bonds are not observed in the present study except for some weak  $\pi$  interactions.

**Table 3** The calculated dipole moment (in D),  $\beta$  components and  $\beta_{tot}$  value of DDO (in electrostatic units).

|                     | ,                       |
|---------------------|-------------------------|
| $\beta_{xxx}$       | -773.119                |
| $\beta_{xxy}$       | -452.348                |
| $\beta_{xyy}$       | 60.064                  |
| $\beta_{vvv}$       | 17.790                  |
| $\beta_{xxz}$       | -14.443                 |
| $\beta_{xyz}$       | 32.529                  |
| $\beta_{vvz}$       | 10.887                  |
| $\beta_{xzz}$       | 13.303                  |
| $\beta_{vzz}$       | 8.671                   |
| $\dot{\beta}_{zzz}$ | 0.189                   |
| $\beta_{\rm tot}$   | $7.077 \times 10^{-30}$ |
| $\mu_x$             | 0.8562                  |
| $\mu_{y}$           | 2.8658                  |
| $\mu_z$             | -0.5319                 |
| $\mu$               | 3.0379                  |

#### 3.9. Theoretical studies

Quantum mechanical calculations are used for predicting the molecular NLO properties of molecules. Hyperpolarizability is a third-rank tensor that can be described by a  $3 \times 3 \times$ 3 matrix. The 27 components of the three-dimensional matrix can be reduced to ten components because of the Kleinman symmetry (Kleinman, 1962; Frisch *et al.*, 2000). It can be given in the lower tetrahedral format,

$$E = E^{0} - \mu_{\alpha}F_{\alpha} - \frac{1}{2}\alpha_{\alpha\beta}F_{\alpha}F_{\beta} - \frac{1}{6}\beta_{\alpha\beta\gamma}F_{\alpha}F_{\beta}F_{\gamma} + \cdots$$
 (5)

where  $E^0$  is the energy of the unperturbed molecule,  $F_{\alpha}$  is the field at the origin of  $\mu_{\alpha}$ , and  $\mu_{\alpha}$ ,  $\alpha_{\alpha\beta}$  and  $\beta_{\alpha\beta\gamma}$  are the components of dipole moment, polarizability and first-order hyperpolarizability, respectively.

$$\beta_{0} = (\beta_{x}^{2} + \beta_{y}^{2} + \beta_{z}^{2})^{1/2}, \text{ and}$$

$$\beta_{x} = \beta_{xxx} + \beta_{xyy} + \beta_{xzz},$$

$$\beta_{y} = \beta_{yyy} + \beta_{xxy} + \beta_{yzz},$$

$$\beta_{x} = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}.$$
(6)

The calculated first-order hyperpolarizability ( $\beta$ ) and dipole momment ( $\mu$ ) of the specimen are 7.077 × 10<sup>-30</sup> electrostatic units (>25 times that of urea) and 3.0379 D, respectively (Table 3). The high value of  $\beta$  is a result of the behaviour of the nonzero  $\mu$  values. In the present study,  $\beta$  is large but SHG is zero. The behaviour of high  $\beta$  with small SHG has been reported for the compound ephendrinium (Sylla *et al.*, 2006). It appears that molecular orientations cancel out charge transfer, resulting in a very low SHG in the crystal. The optimized structure of DDO is given in Fig. 8(*b*) and it closely resembles the displacement ellipsoid diagram (Fig. 8*a*).

#### 4. Conclusions

Transparent crystals of 1,5-diphenylpenta-2,4-dien-1-one were grown in ethanol by the slow evaporation solution growth technique at room temperature. The product formation was confirmed by FT–IR, FT–Raman and single-crystal XRD analyses. The powder X-ray diffraction study shows the good crystallinity of the material. TG/DSC studies reveal the purity of the sample and no decomposition is observed up to the melting point. Good transmission in the entire visible region is observed with a band gap energy of 2.87 eV as estimated by diffuse reflectance spectroscopy. HRXRD studies reveal a low-angle structural grain boundary. The high first-order hyperpolarizability with zero SHG could be attributed to orientation factors. The halogen-substituted chalcones exhibit a high SHG efficiency.

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