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THE GROWTH AND CHARACTERIZATION OF 2,4-DINITRO PHENYL HYDRAZONE OF BENZOPHENONE AND MIXED CRYSTALS

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Good quality benzophenone (BP) crystals were grown by solution technique using $CHCl_3$ as solvent by adopting slow evaporation method at room temperature. The grown crystals were subjected to various characterization studies to analyze its purity and applications. The condensation product 2,4-dinitro phenyl hydrazone of benzophenone (DNPBP) was prepared by adopting standard procedure. Then mixed crystal of BP and DNPBP was also grown by solution growth. Both the condensation product and mixed crystals were characterized by UV, FTIR, ^{1}H NMR spectra. Thermal (TG and DTA) studies have proved to be very useful techniques not only to study the thermal properties of BP, DNPBP and mixed crystal but also to study their purity. Second harmonic generation (SHG) efficiency of the grown crystals was determined.

Keywords: *benzophenone, characterization, DTA, mixed crystal, SHG efficiency, solution growth, TG*

Introduction

Organic non linear optic materials have greater importance due to their high non linear optical properties, rapid response in electro optic effect and large second or third order hyper polarisabilities compared to inorganic NLO materials. In recent years considerable interest has developed in the study of organic compound exhibiting NLO properties [1]. Benzophenone is one such material. NLO property of benzophenone and its derivative have been studied using powder SHG method. The results show several of these compounds generate SHG signals stronger than that of urea [2, 3]. According to the literature, the benzophenone single crystal were first grown by the Czochralski technique [4] followed by reports from the solution method [5] and Bridgmann technique [6]. The study of band gap measurement of solution grown benzophenone was recently reported [7]. Vijayan *et al.* [8] reported the growth of semicarbazone of benzophenone by slow evaporation solution growth technique. Semicarbazone of acetophenone was grown by slow evaporation technique and the grown crystals were characterized by X-ray, FTIR, UV-visible spectral analysis [9]. Many authors have investigated various organic compounds due to their chemical, biological and environmental importance and also examined their various properties [10–47]. The aim of this paper is the detailed study of the growth of BP and mixed crystals of BP and DNPBP.

Experimental

Materials

Crystal growth of benzophenone

The analar grade benzophenone was purified by repeated recrystallization from $CHCl_3$ as solvent. The pure crystals of benzophenone were taken for crystal growth. The saturated solution of benzophenone was prepared in $CHCl_3$. It was allowed for slow evaporation at room temperature. Good transparent crystals were obtained in three to four days. These crystals were harvested and subjected to various characterization studies.

Solubility

The solubility of benzophenone was measured in various temperature ranges. The temperature of the solution was maintained above the chosen constant temperature and continuously stirred to ensure homogenous temperature and concentration throughout the entire region of the solution. A volume of 50 mL of

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$CHCl_3$ was taken in a container and recrystallized BP was added once the saturation was reached, the equilibrium concentration of the solute was analyzed gravimetrically. The experiment was repeated for various temperatures from room temperature to 40°C in steps of 2°C. Solubility determination shows that the solubility increases with temperature. This is evidenced by the solubility curve shown in Fig. 1.

Metastable zone width

In order to determine metastable zone width of the solutions, conventional method was employed. The solution of benzophenone in $CHCl_3$ saturated at 30°C was cooled from slightly overheated temperature at a constant cooling rate till the first visible crystal was observed. Uniform concentration gradient was achieved by stirring the solution. The temperature difference between the saturation and nucleation temperature of the experimental solution was determined as its metastable zone width. The same procedure was adopted to measure the metastable zone width of benzophenone for different temperatures viz 32, 37 and 40°C. From the values of solubility, saturation temperature and nucleation temperature, the metastable zone width is determined and shown in Fig. 1.

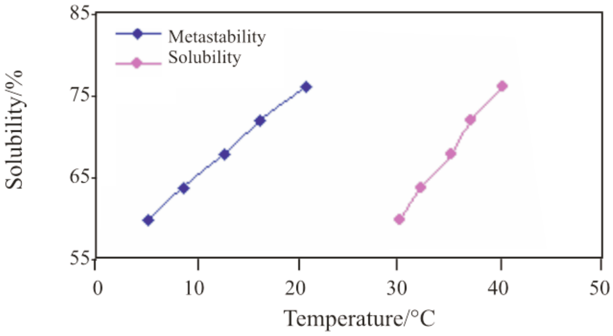


Fig. 1 Solubility and metastability of benzophenone in $CHCl_3$

Preparation of 2,4-dinitro phenylhydrazone of benzophenone

5 g 2,4-dinitrophenyl hydrazine was suspended in 10 mL of methanol. To this solution, 0.5 mL of concentrated sulphuric acid was added cautiously. The warm solution was filtered and a solution of 0.5 g of benzophenone was added in small volume of methanol. Solid separates within five minutes. The solid derivative was separated and washed with aqueous methanol. The melting point of the derivative was found to be 237°C.

$$\underset{\text{BP}}{(C_6H_5)_2C{=}O}+C_6H_3(NO_2)_2NH{-}NH_2 \xrightarrow{\text{conc. } H_2SO_4}$$

$$\underset{\text{DNPBP}}{(C_6H_5)_2C{=}N{-}NH(NO_2)_2H_3C_6}$$

Crystal growth of mixed crystal

Saturated solutions of benzophenone and 2,4-dinitrophenyl hydrazone of benzophenone were prepared in $CHCl_3$. These two saturated solutions were mixed thoroughly and allowed for slow evaporation at room temperature. Good transparent mixed crystal of BP and DNPBP obtained in one to two days. These crystals were harvested and subjected to various characterization studies.

Methods

TG and DTA analysis

Differential thermal analysis (DTA) and thermogravimetric analysis (TG) were carried out on the crystal samples for qualitative analysis. These studies were conducted for benzophenone, mixed crystal and DNPBP samples. Both TG and DTA were carried out on a Netzsch STA 409 simultaneous thermal analyses using alumina crucible in nitrogen atmosphere in the temperature range of 28 to 1000°C and heating rate 10°C min^{-1}.

FTIR spectra

The FTIR spectrum was recorded in the range of 400–4000 cm^{-1} for BCAP sample on an AVATAR330 FTIR spectrophotometer using KBr pellet technique.

UV absorbance spectra

UV visible spectrophotometer (Version 02.00) was used to record the UV visible spectra of the grown crystals.

^{1}H NMR spectrum

The ^{1}H NMR spectrum has been recorded for the benzophenone in $CDCl_3$ at 400 MHz using a JEOL instrument.

Results and discussion

UV absorbance spectra

Since BP crystal is colourless, the absorption is not observed between 400 to 800 nm, which is shown in Fig. 2. The maximum absorption is at 347 nm due to C=O group. The DNPBP is coloured compound. Therefore, the absorption is observed between 400 to 799 nm. The maximum 250 nm absorption is assigned to C=N which is shown in Fig. 3. Mixed benzophenone is coloured compound. Hence the absorption is observed at 400 to 800 nm. The presence of C=N and

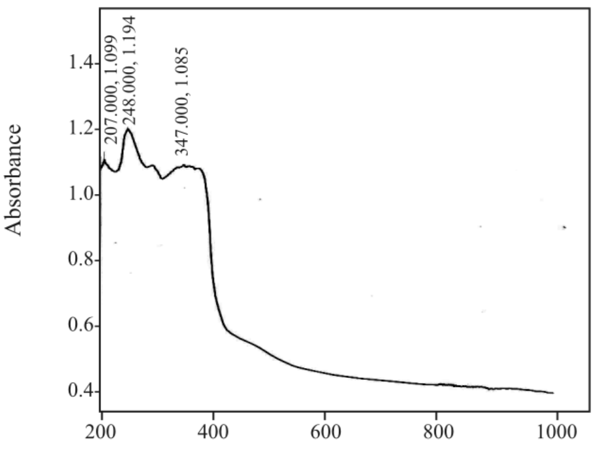


Fig. 2 UV Absorbance spectrum of BP

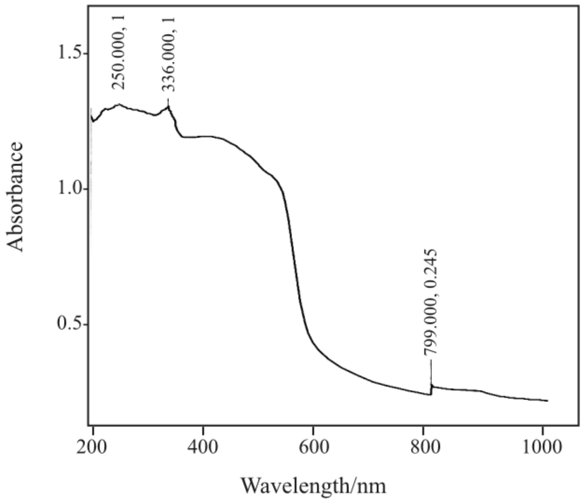


Fig. 3 UV Absorbance spectrum of DNPBP

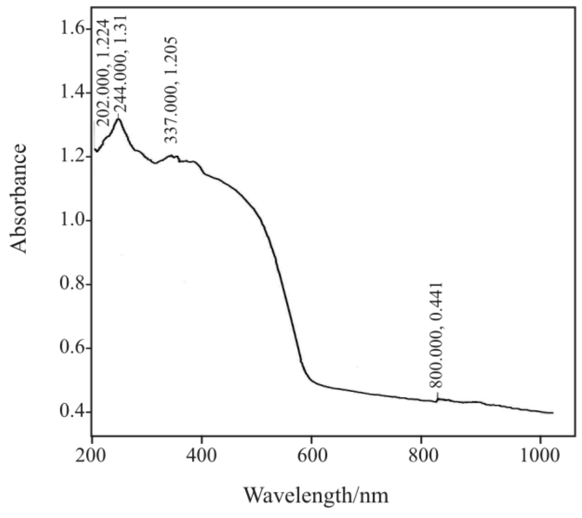


Fig. 4 UV Absorbance spectrum of mixed crystal

N–H group absorptions were at 244 and 337 nm, which is shown in Fig. 4. Generally C=N groups are coloured. The resonance interactions between C=N and aromatic rings could provide more resonance energy.

FTIR spectral analysis

Infrared spectrum is an important record, which provides information about the structure of a compound. In this technique almost all functional groups in a molecule absorb characteristically within a definite range of frequency. The absorption of IR radiation causes the various bands in a molecule to stretch and bend with respect to one another. The most important region (4000–650 cm^{-1}) is of prime importance for the study of an organic compound by spectral analysis [48]. The FTIR spectrum of benzophenone was scanned 400 to 4000 cm^{-1}. The C=O group is found at 1650 cm^{-1}. The aromatic skeletal vibration is at 1447 cm^{-1}. The C-H deformation is found at 935 cm^{-1}. The FTIR spectrum of DNPBP was also scanned in the same spectral region. The NO_2 group stretching is assigned to 1444 cm^{-1}. The N–H deformation is found at 1558 cm^{-1}. The C=N stretching is observed at 1689 cm^{-1} and the NO_2 asymmetric stretching is at 1540 cm^{-1}. The NO_2 in aromatic compound symmetric stretching is found at 1361 cm^{-1}. The NO_2 deformation is found at 596 cm^{-1} and the phenyl ring deformation is observed at 717 cm^{-1}.

The FTIR spectrum of mixed crystal in higher wave number region gives interesting information with regard to bonding of the groups in the crystal. The doublet at 800 cm^{-1} in the spectrum is the characteristic of the aromatic 1,4-substitution. A strong singlet peak is observed at 1080 cm^{-1} also represents the same. Weak and variable peaks observed at 1160 and 1440 cm^{-1}, respectively, further support the presence of aromatic 1,4-substitution. The variable strong doublet peak in the frequency range 1275–1300 cm^{-1} gives the presence of conjugated NO_2 group. The variable doublet peak at 1560 and 1580 cm^{-1} shows the stretching of aromatic C=N. The two peaks observed at 2805 and 2950 cm^{-1} support the aromatic C–H stretching. The C=O carbonyl stretching is at 1650 cm^{-1}. The aromatic ring skeletal vibration is at 1447 cm^{-1} and the C=N group is at 1593 cm^{-1}. The peaks below 1500 cm^{-1} are due to C=N and N–H bending. The peaks lying between 3200 to 3000 cm^{-1} is due to N–H and C–H stretching.

^1H NMR spectrum

The ^1H NMR spectrum was recorded for the benzophenone in $CDCl_3$ at 400 MHz in JEOL instrument shown in Fig. 5 showed multiplet of 14 peaks in the

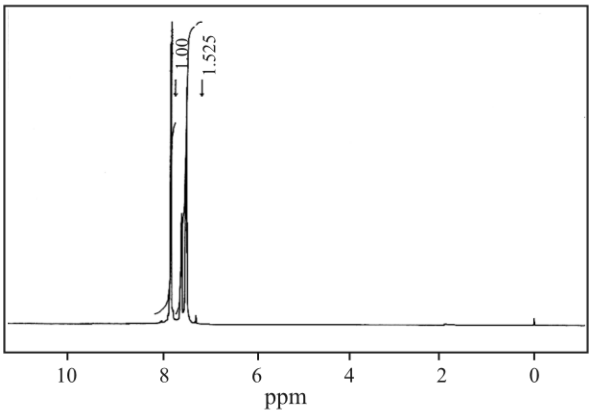
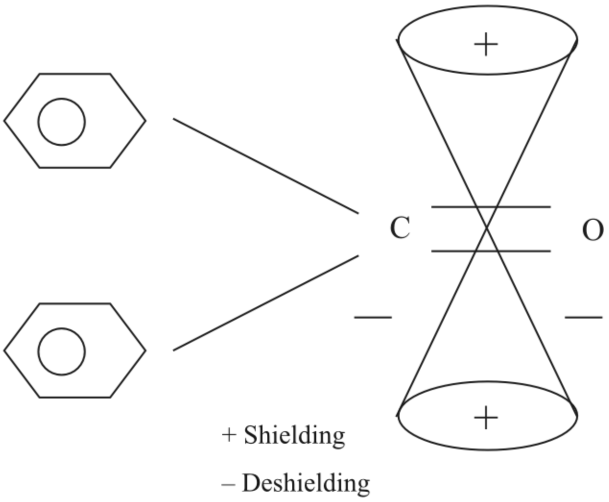


Fig. 5 ^{1}H NMR spectrum of BP

aromatic region. All the ten protons of two phenyl rings are in the deshielding region of both the carbonyl group and the benzene ring. Here the two-phenyl ring and the carbonyl group are in a same plane and hence all the protons are neighbouring. Radio frequency is in the down field region between 7.2476 and 7.8448 ppm. If there is any deviation from the planarity, a few protons of one phenyl ring may go to the shielding region of other benzene ring and vice versa and show low delta value.



The ^{1}H NMR spectrum of 2,4-dinitro phenylhydrazone of benzophenone in $CDCl_3$ at 400 MHz was also recorded using the same instrument and is given in Fig. 6 and showed peaks in the aromatic region. Radio frequency in the down field region is between 7.2610 and 7.8168 ppm for benzophenone. The singlet appearing at delta 1.595 ppm is due to the NH proton. The radio frequency in the up field region 8.2064 to 11.2354 ppm is due to the presence of dinitrobenzophenone group. The doublet at 9.1 ppm is assigned to 2,4-dinitro phenyl (3-H). The doublet at 8.3 to 8.4 ppm is assigned to 2,4-dinitro phenyl (5-H) and the doublet at 8.2 ppm is assigned to (6-H).

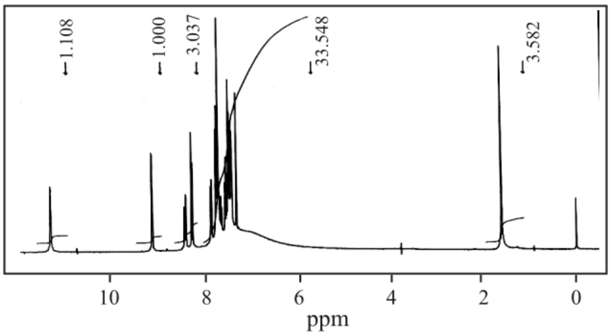


Fig. 6 ^{1}H NMR spectrum of DNPBP

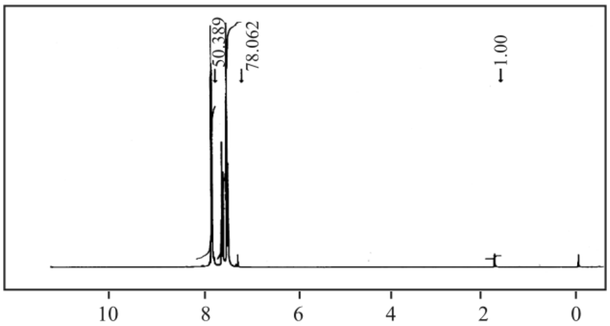


Fig. 7 ^{1}H NMR spectrum of mixed crystal

^{1}H NMR of mixed crystal was also recorded in $CDCl_3$ at 400 MHz using the same instrument is given in Fig. 7 and showed few more peaks in the aromatic region along with one singlet in the non-aromatic region confirmed that DNPBP was mixed with benzophenone. The singlet appearing at delta 1.7820 ppm is due to the NH proton. Generally the NH proton of aromatic compound absorb in 5 to 3 ppm due to the formation of H-bonding. In this case the proton of nitro substituents on the phenylhydrazone part due to the electron with drawing nature pulls the electron cloud from the benzophenone part. Here these electron densities around the NH proton increased which accounts for the up field shift of the NH signal due to high shielding of NH-proton.

XRD studies

The high resolution GUINIER powder X-ray diffractometer (CSEIFERT, Germany) with CuK_α radiation has been used for X-ray diffraction studies. The predominant X-ray diffraction pattern of solution grown benzophenone shown in Fig. 8, is in good agreement with the JCPDS values and standard values.

The predominant peaks are (0 2 1), (2 1 0), (0 1 2), which are in accordance with the literature values [49]. Further, the narrow and strongest peak along (0 2 1) direction confirms the single crystalline nature of the solution grown benzophenone (Fig. 9).

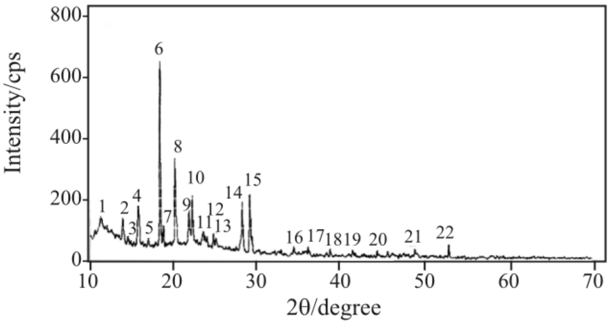


Fig. 8 XRD pattern of benzophenone

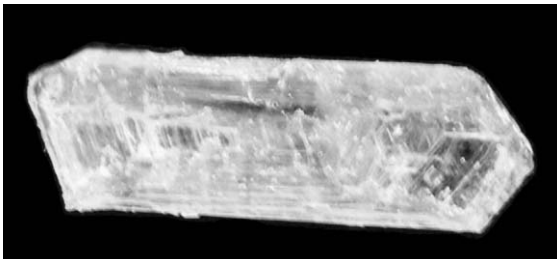


Fig. 9 Benzophenone crystal grown from $CHCl_3$

Thermal (TG and DTA) studies

The mass change in the sample with temperature was studied by TG and the energy change in the sample with temperature was studied by DTA. The analysis was performed in nitrogen atmosphere. The TG and DTA curves of solution grown BP are given in Fig. 10. There is an intense single stage mass loss at 272.5°C with a total mass loss of 98.85% is observed in the TG curve of benzophenone. DTA curve is also shown in Fig. 10 shows a sharp peak at 49°C due to the melting point. In the TG curve of DNPBP (Fig. 11) there is an intense single stage mass loss at 112 to 478°C with a DTA exothermic peak maximum at 272°C. The total mass loss corresponds to 98.28%.

The TG-DTA curves of mixed crystal are shown in Fig. 12. The TG curve in Fig. 12 shows an intense single stage mass loss in the region from 160 to 270°C while the DTA curve shows a broad exothermic peak in the same region with maxima at 225°C. The total mass loss corresponds to 98.87%. A sharp peak observed in DTA at 60°C is due to melting.

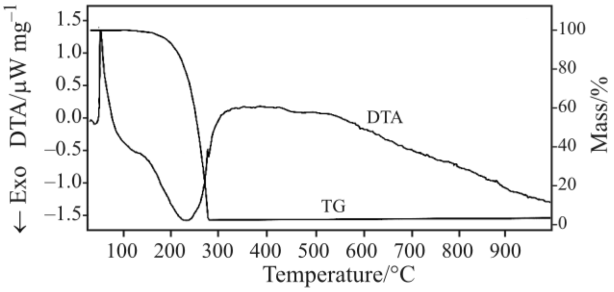


Fig. 10 TG and DTA curves of solution grown BP

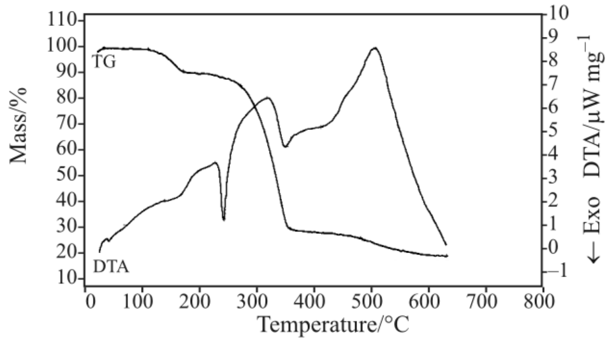


Fig. 11 TG and DTA curves of DNPBP

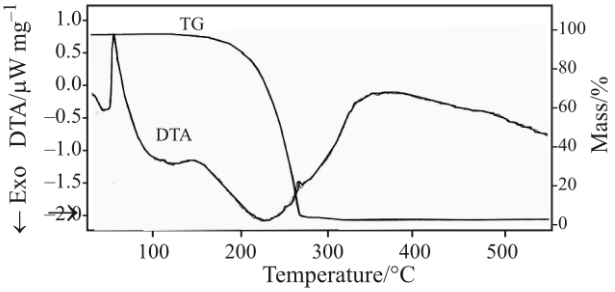


Fig. 12 TG and DTA curves of mixed crystal

Second harmonic generation (SHG) efficiency

Second harmonic generation test on the crystals were performed by Kurtz powder SHG method [50]. An Nd:YAG laser with a modulated radiation of wavelength 1064 nm was used as the optical source and directed on the powdered sample through a filter. The SHG efficiency of BP is found to be 81. It is 0.54 times SHG efficient compared to KDP crystals. The SHG efficiency of mixed crystal is 96. It is found to be 0.64 times efficient compared to KDP crystals. It is clear evidence that mixed crystal has higher NLO property.

Conclusions

Good quality benzophenone and benzophenone mixed with DNPBP crystals were grown by solution growth technique using slow evaporation method. The grown crystals were analysed using UV, FTIR, ^{1}H NMR, XRD, TG and DTA studies. The metastable zone width of benzophenone in $CHCl_3$ was determined.

TG and DTA studies shows the similar trends between BP and mixed crystal but there is a significant difference with the TG and DTA studies of DNPBP. XRD result confirms the single crystalline nature of the solution grown benzophenone. The presence of C=N group in mixed crystal, C=O group in BP and N–H group in DNPBP are confirmed by FTIR spectrum. The NMR spectrum of benzophenone and doped benzophenone crystals shows important absorption peaks which corresponds to functional groups containing different chemical environments. Determination of peak areas in the spectrum reveals the number of protons responsible for each signal. The ratio of peak height in the two triplets due to the protons of two rings are not symmetrical because of the fact that the separation between these two signals is not very large relative to the separation of peaks within a particular triplet. In the recorded NMR spectrum of benzophenone and doped benzophenone, the reason for the appearance of the signal corresponds to N-H proton, aromatic proton in the down field is due to the deshielding effect created by the NO_2 group on these protons. The ^{1}H NMR spectrum shows the presence of C=O and benzene ring in benzophenone.

When 2,4-dinitrophenyl hydrazone of benzophenone is incorporated in the crystals of benzophenone, the C=O is replaced by C=N group which causes the delocalisation of the electron clouds so as to increase asymmetric unit. Thus we expect the enhancement of dipole moment resulting in the increase of the NLO property of mixed crystal. The SHG efficiencies of BP and mixed crystal are 81 and 96, respectively. It is clear evidence that mixed crystal has higher NLO property.

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