

# Crystal growth and investigation of efficient non-linear optical materials in the mixed (2,-4-dinitrophenyl)-L-alanine (DPA) and 2-methyl-4-nitroaniline (MNA) system

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When a 1:1 weight mixture of (2,-4-dinitrophenyl)-L-alanine (DPA) and 2-methyl-4-nitroaniline (MNA) is dissolved in a 50:50 volume mixture of ethyl acetate and hexane, two types of crystals were observed on slow evaporation. In the first stage of crystallization, light-yellow plates of MNA measuring up to 25 mm × 5 mm × 1 mm were formed, which belong to the triclinic space group P1 with lattice parameters  $a = 0.7621(3)$  nm,  $b = 0.7952(5)$  nm,  $c = 0.8200(2)$  nm,  $\alpha = 111.84(2)^\circ$ ,  $\beta = 93.76(2)^\circ$ ,  $\gamma = 116.84(3)^\circ$ ,  $Z = 2$ . The volume of the unit cell containing two molecules is  $361.9(1) \times 10^{-3}$  nm<sup>3</sup>. The powder SHG efficiency of the triclinic polymorph (MNA(T)) is about the same as that of the monoclinic MNA(M). The Raman spectrum of the new crystal is similar to that of MNA(M) crystallized from the vapour phase or solution, except for the change in the intensity of a few bands. The DSC data show minor differences in the melting points and specific heats for the two phases. The second stage of crystallization resulted in the formation of orange–yellow coloured crystals of the DPA:MNA complex, in the monoclinic space group P2<sub>1</sub> with lattice parameters  $a = 0.6876(1)$  nm,  $b = 0.7621(3)$  nm,  $c = 1.7626(4)$  nm,  $\beta = 96.62(2)^\circ$ ,  $V = 917.5 \times 10^{-3}$  nm<sup>3</sup>,  $Z = 2$  for C<sub>16</sub>H<sub>17</sub>N<sub>5</sub>O<sub>8</sub>. The Raman spectrum of DPA:MNA consists of bands from both DPA and MNA. The complex melts at 138(1)°C with a specific heat of 25.3(4) cal g<sup>-1</sup> according to the DSC measurements. The powder SHG efficiency is nearly the same as that of methyl-(2,4-dinitrophenyl)-aminoproanoate (MAP).

## 1. Introduction

Several organic materials have been investigated because of their exceptional non-linear optical (NLO) properties [1–8]. Among these, 2-methyl-4-nitroaniline (MNA) is reported to have one of the largest second-order non-linear coefficients,  $\chi^{(2)}$  ( $d_{12} = 38$  and  $d_{11} = 250$  pm V<sup>-1</sup>) [7]. MNA has been reported to crystallize in the monoclinic group Cc [9], and large crystals of MNA are difficult to grow from solution as well as from the melt. In an effort to improve the morphology of the MNA crystals, we have attempted to grow mixtures of MAP and MNA [10]. The result was an equimolar complex crystallizing in the space group P2<sub>1</sub> with lattice parameters different from those of either MAP or MNA [11]. It was felt that the new band at 540 nm, observed in the

absorption spectrum of the mixed crystal, which may be due to packing effects, was responsible for the reduced second harmonic generation (SHG) efficiency [10]. Therefore, MAP was substituted by the precursor in its synthesis, namely, (2,-4-dinitrophenyl)-L-alanine (DPA) [12]. A 1:1 by weight mixture of DPA and MNA was dissolved in a 50:50 volume mixture of ethyl acetate/hexane (EH solvent). On slow evaporation, two different types of crystal were observed. One was light-yellow in colour and the other orange–yellow. The light-yellow crystals were found to be a triclinic polymorph, MNA(T) of MNA, and the orange–yellow crystals were due to complex of DPA and MNA, crystallizing in the monoclinic space group P2<sub>1</sub>. The crystal growth and properties of these two types of crystal are presented below.

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## 2. Experimental procedure

### 2.1. Starting materials

Commercial MNA (Aldrich Chemical) was purified by physical vapour transport using oxygen as the carrier gas.

DPA was synthesized in the laboratory following Sanger's method, described by Oudar and Hierle [12]. It exhibits an intense SHG in the powder form similar to MAP but is difficult to crystallize.

### 2.2. Crystallization of DPA:MNA mixtures

DPA and MNA, 1:1 by weight, were dissolved in the EH solvent while heating it to 40 °C in a covered conical flask. The hot solution was filtered into crystallization dishes. These dishes were covered with tight-fitting perforated lids and the solutions were allowed to evaporate slowly. After nearly 25–30 h, two types of crystal were observed in the dishes, namely, light-yellow plate-like crystals growing at the bottom of the solution and orange-yellow nodules growing along the walls. These two types of crystals were separated carefully and dissolved again in the EH solvent at 35 °C in different covered conical flasks. On slow cooling and evaporation of the solutions, transparent, light-yellow plate-like crystals, measuring up to 25 mm × 5 mm × 1 mm were observed in the solution made from the light-yellow plate-like crystals. The orange-yellow nodules crystallized in the form of small, transparent, orange-yellow plates measuring up to 2 mm × 1 mm × 1 mm, but in bunches. It was very difficult to grow sufficiently large crystals of this; therefore, the small crystals were separated and used for the investigations. In addition, it was observed that the crystals of MNA, grown in the presence of DPA, grew much larger than those prepared from the same solvent mixture without DPA. A detailed investigation of the crystals grown with and without DPA may help us to understand the role that DPA plays in the polymorphic growth. The physical and optical proper-

ties of these crystals are presented in the following section.

## 3. Results

### 3.1. Crystal structure

The crystal structure (Fig. 1) of the light-yellow crystals was determined using a four-circle X-ray diffractometer with MoK $\alpha$  X-radiation. Detailed X-ray diffraction (XRD) analysis of the light-yellow plates confirmed them to be a triclinic polymorph of MNA in the space group P1 [13]. The lattice parameters are  $a_t = 0.7621(3)$  nm,  $b_t = 0.7952(5)$  nm,  $c_t = 0.8200(2)$  nm,  $\alpha = 111.84(2)^\circ$ ,  $\beta = 93.76(2)^\circ$ ,  $\gamma = 116.84(3)^\circ$ ,  $V = 361.9(1) \times 10^{-3}$  nm<sup>3</sup>,  $Z = 2$  for C<sub>7</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>, with 1270 reflections observed.

The crystal structure of MNA(T) was solved by direct methods. The packing of MNA(T) is almost identical to that of the published monoclinic structure [8,9], which we called MNA(M), whose data are: space group 1a, lattice parameters  $a_m = 0.8225(1)$  nm,  $b_m = 1.1620(1)$  nm,  $c_m = 0.7585(2)$  nm,  $\beta = 94.08920^\circ$ ,  $V = 723.1 \times 10^{-3}$  nm<sup>3</sup>,  $Z = 4$  for C<sub>7</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub> [9]. A 4 × 4 transformation matrix for the monoclinic to triclinic unit cell was obtained, as shown in the matrix equation

$$(a'_m b'_m c'_m) = (a_t b_t c_t) \begin{vmatrix} 0 & -1 & -1 & -0.5051 \\ 0 & -2 & 0 & 0.2416 \\ -1 & -1 & 1 & 0.5243 \\ 0 & 0 & 0 & 1 \end{vmatrix} \quad (1)$$

The calculated monoclinic cell for MNA(T), and the deviations,  $\Delta$ , from the monoclinic cell given elsewhere [9] are  $a'_m = 0.8200$  nm ( $\Delta = -0.0025$  nm),  $b'_m = 1.1610$  nm ( $\Delta = -0.0010$  nm),  $c'_m = 0.7621$  nm ( $\Delta = -0.0036$  nm),  $\alpha = 90.48^\circ$  ( $\Delta = 0.48^\circ$ ),  $\beta = 93.76^\circ$  ( $\Delta = -0.32^\circ$ ),  $\gamma = 89.86^\circ$  ( $\Delta = 0.14^\circ$ ). For the triclinic

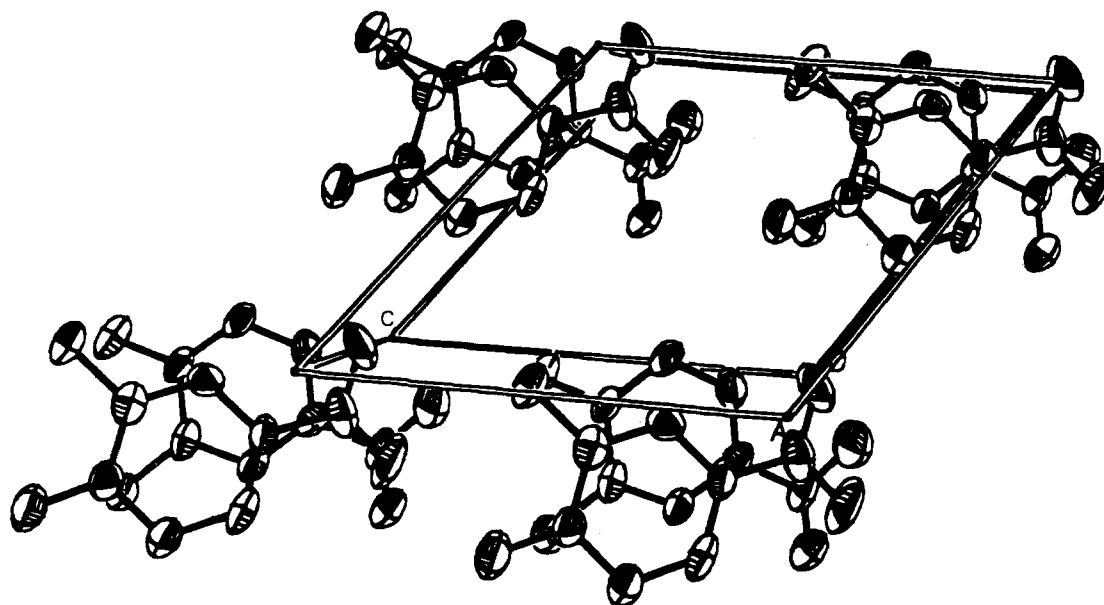


Figure 1 The unit cell of MNA(T). The two MNA molecules stack along the *a*-axis.

data of MNA(T), refined in space group, P1, the agreement factor,  $R$ , is about 6%; one can also refine both the original monoclinic data and the new triclinic data in both space groups, with roughly equivalent results. However, about 20 new reflections of moderate intensity are observed in the new P1 data set for MNA(T) that are systematically absent in the MNA(M) data set of Lipscomb *et al.* [9]. We speculate that this is a new polymorph, formed in the presence of DPA in solution, which is supported by the experimental results given in the following sections.

The DPA:MNA complex is observed to crystallize in the monoclinic space group  $P2_1$  with lattice parameters  $a = 0.6876(1)$  nm,  $b = 0.7621(3)$  nm,  $c = 1.7626(4)$  nm,  $\beta = 96.62(2)^\circ$ ,  $V = 917.5 \times 10^{-3}$  nm<sup>3</sup>,  $Z = 2$  for  $C_{16}H_{17}N_5O_8$ . The structure was solved by direct methods and refined with isotropic temperature factors to  $R = 15\%$ , and it is shown in Fig. 2. It is quite clear that in DPA:MNA there is not much  $\pi$ - $\pi$  overlap between the aromatic planes of DPA and MNA; the structure is dominated by the coplanar hydrogen bonds between the amino group of MNA and the nitro group of DPA: the same structural motif as in MAP:MNA [10].

### 3.2. Second harmonic generation

The SHG efficiencies of the crystals were evaluated by placing the powder of the crystals between two glass slides, and exposing it to the 1064 nm beam from a pulsed Nd:YAG laser (Spectra Physics) using an apparatus similar to that described by Okomoto *et al.* [14]. An intense green emission was observed from the MNA(T). A comparison was made of the SHG emission from the commercial MNA powder, MNA crystallized in EH solvent, and MNA crystallized in the EH solvent in the presence of DPA. It was found that the SHG intensities of the three were about the same. The intensity of the SHG of DPA:MNA complex was observed to be close to that of MAP, but much less than that of MNA. However, it may be pointed out that the powder method is not an accurate method to obtain the non-linear optical parameters [15]. We have used this method to ascertain whether or not the

material is phase matchable and also for a quick assessment of the usefulness of the materials for NLO applications before the growth of large crystals is attempted.

### 3.3. Optical absorption

The optical absorption spectrum was recorded using a Perkin-Elmer spectrophotometer (model 323) in the range 450–2000 nm. A typical spectrum of the triclinic MNA(T) crystal plate shows a broad absorption band from 480–650 nm (see Fig. 3), which was confirmed by studying crystals grown in different crystal growth runs. However, sufficiently large plates of DPA:MNA were not available for the optical absorption measurements.

### 3.4. Raman spectra

The Raman spectra, recorded with the  $Ar^+$  514.5 nm excitation as described earlier [16], were employed to determine the molecules present in the crystals [10]. The spectrum of triclinic MNA(T) is almost identical, except for a few bands, to that of the spectra of monoclinic MNA(M) in the form of powders, vapour-grown crystalline plates, and crystals obtained by slow evaporation of the EH solution containing MNA. The Raman spectra of an MNA(T) crystal grown in the presence of DPA and an MNA(M) crystal grown from the vapour phase are compared in Fig. 4. The Raman spectrum of the DPA:MNA crystal shows bands that correspond to DPA in addition to those of MNA as shown in Fig. 5. The various Raman bands that occur in DPA, MNA and DPA:MNA are given in Table I for comparison.

### 3.5. Melting point and specific heat measurements

The melting points and specific heats of the materials were determined by differential scanning calorimetry (DSC) as described earlier [10]. Samples weighing 6–10 mg were used for each experiment, and each measurement was repeated at least three times to

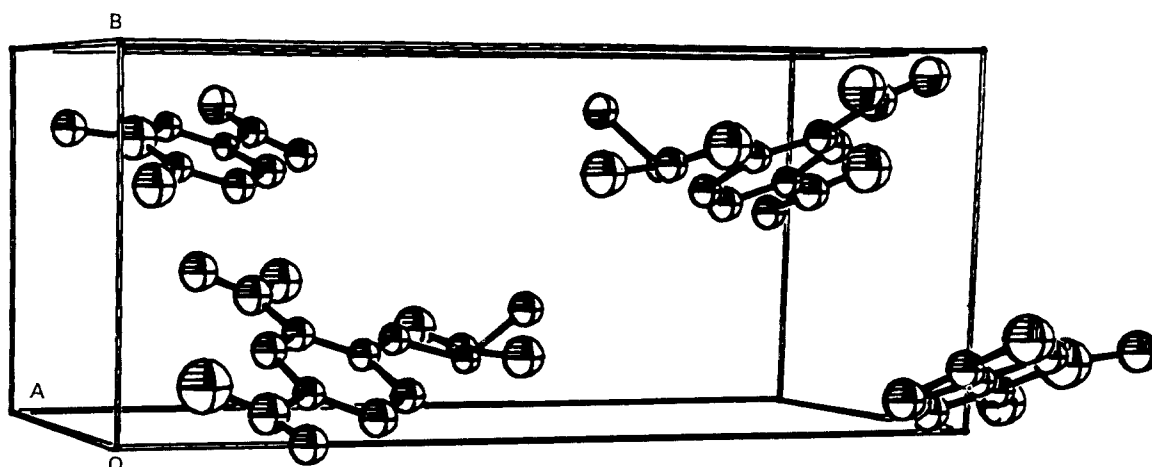


Figure 2 The unit cell of DPA:MNA complex.

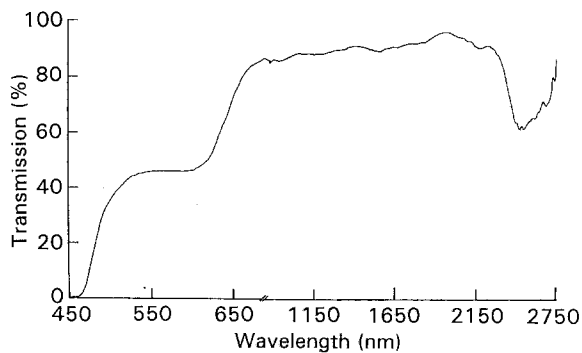


Figure 3 Optical absorption spectrum of MNA(T) in the range 450–2600 nm. An absorption is seen from 480–600 nm.

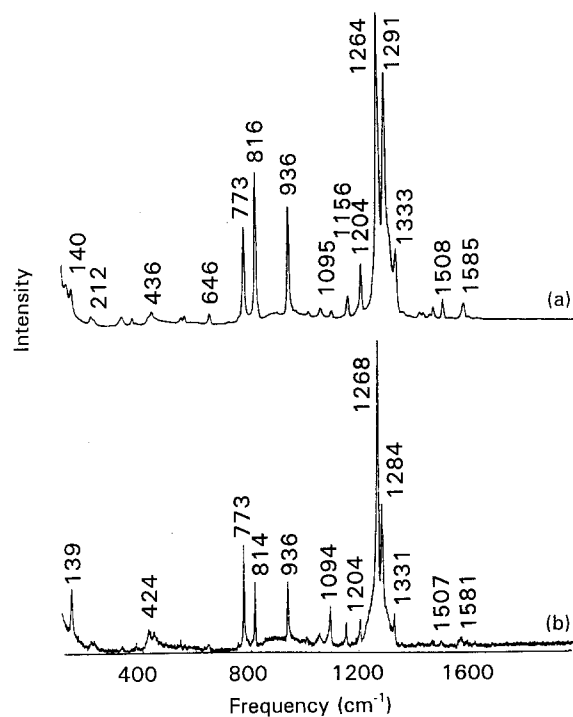


Figure 4 Raman spectrum of (a) MNA(T) and (b) MNA(M).

confirm reproducibility. The DSC curves for the MNA, DPA and DPA:MNA are presented in Fig. 6, and the results are summarized in Table II.

#### 4. Discussion

Lipscomb *et al.* [9] determined the crystal structure of MNA using crystals grown from a mixture of 50% *o*-xylene and 50% methanol and reported it to be monoclinic with four molecules per unit cell. With two molecules per unit cell, the polymorph, MNA(T) (Fig. 1), has nearly the same *V/Z* ratio as the MNA(M). In MNA(T) the crystallographically distinct MNA molecules MNA(1) and MNA(2) stack approximately along the *a*-axis with the least squares benzene planes forming a dihedral angle of 4.5° with each other. These planes are slanted at 21° and 31°, respectively, to the *a*-axis. The MNA(1) and MNA(2) overlap is staggered; the centre of the benzene ring of MNA(1) lies below the benzene ring carbon atom of MNA(2) that is bonded to the methyl carbon. The vector connecting the two nitrogen atoms in MNA(1)

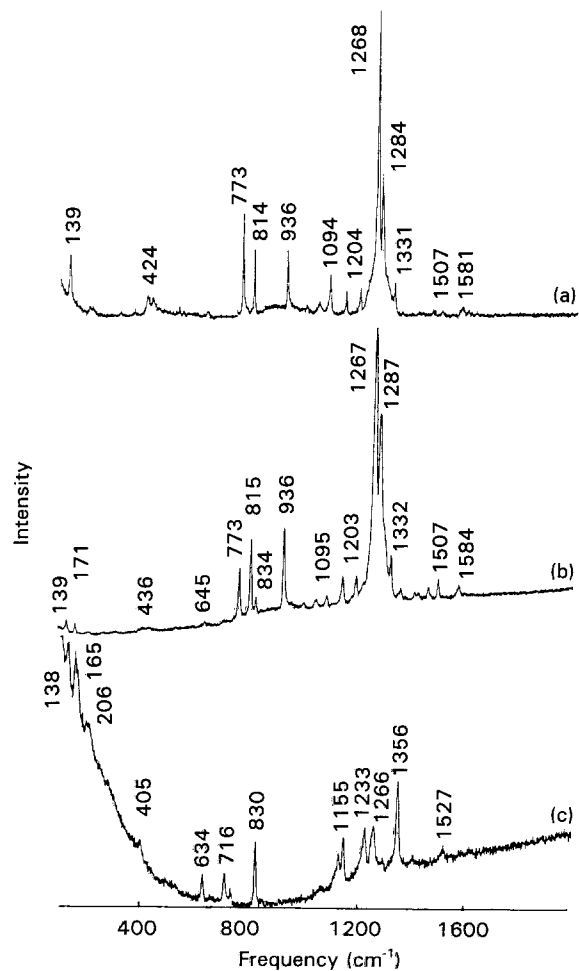


Figure 5 Raman spectrum of (a) MNA(M), (b) DPA:MNA complex, and (c) DPA.

TABLE I Correlation between the observed Raman bands ( $\text{cm}^{-1}$ ) of DPA:MNA complex with those of the parent compounds DPA and MNA

DPA	DPA:MNA	MNA
138	138	139
165	171	–
634	645	646
716	740	–
739	–	–
–	773	773
–	815	814
830	834	–
–	936	936
1050	1052	–
1095	1095	1094
1137	–	–
1155	1150	1153
–	1203	1204
1266	1267	1268
–	1287	1284
–	1332	1331
1356	1365	–
–	1430	–
–	1467	–
1527	1507	1507
–	1584	1581
–	1618	–

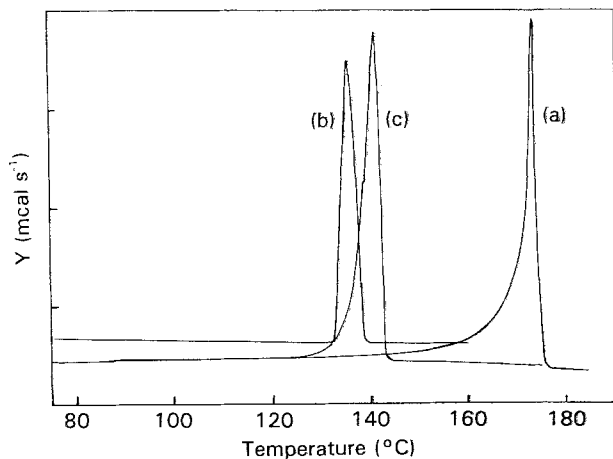


Figure 6 Melting point curves of (a) DPA, (b) MNA, and (c) DPA:MNA complex. The maximum range is  $Y = 5$  for DPA, 15 for MNA, and 8 for DPA:MNA.

TABLE II Thermal analysis data of DPA, DPA:MNA

Compound	MNA(M)	MNA(T)	DPA	DPA:MNA
Peak ( $^{\circ}\text{C}$ )	135(1)	135(1)	171(2)	141(1)
Onset (m.p.) ( $^{\circ}\text{C}$ )	133(1)	132(1)	169(2)	138(1)
Specific heat ( $\text{cal g}^{-1}$ )	39.2(2)	37.2(2)	20.5(5)	25.3(4)

forms an angle of about  $60^{\circ}$  with the corresponding N–N vector of MNA(2) (so that the molecular dipoles are in approximate addition). Both oxygen atoms of MNA(1) (MNA(2)) are within the hydrogen bonding distance of the methyl group hydrogens of MNA(2) (MNA(1)). The stacking is remarkably similar to that of MNA(M). However, the molecular orientation in MNA(T) appears to be more favourable for efficient phase-matched SHG from the crystal. The phase matching directions have to be identified.

This difference in the molecular orientation appears to be causing minor differences in the relative in-

tensities and the frequencies of the bands in the Raman spectra. For example, in the case of the MNA(T), the  $816$  and  $936\text{ cm}^{-1}$  bands are stronger than the  $773\text{ cm}^{-1}$  band, whereas in the case of MNA(M), the reverse is true. The difference in the molecular orientation may also be responsible for the absorption observed at  $480\text{--}650\text{ nm}$  for MNA(T), which is not observed in the case of MNA(M) [8]. The proximity of the molecules may introduce a small but observable absorption, probably due to charge transfer transitions.

The DSC data shown in Table II also reflect the structural difference in the two compounds by small differences in the melting points and specific heats.

The type of polymorphism discussed above has also been observed in other organic molecules such as *N*-(2-acetamido-4-nitrophenyl)pyrrolidene (PAN) [17], as the growth rates of the crystals were varied. Such changes can be reversed when the crystals go through a temperature cycle. In the present case, however, the growth rates do not appear to affect the polymorphism. It might be influenced by the acidic nature of DPA which may be present in the solution in small amounts.

The chemical structures of MNA, DPA and MAP are shown in Fig. 7. The crystal structure of DPA is not available in the literature. Extensive efforts by us to grow crystals of DPA have not yielded results so far; therefore, the crystal structure could not be obtained in the present work. The difference between DPA and MAP is the substitution of the hydrogen in the carboxylic group of DPA with  $\text{CH}_3$ . The mixture of DPA:MNA always resulted in small but well-formed, transparent orange–yellow coloured crystals. Preliminary crystal structure analysis indicates that this is also an equimolar complex like the MAP:MNA reported earlier [10].

The XRD data, the Raman and thermal analysis results, indicate that both parent molecules are present in the mixed DPA:MNA crystals. The Raman spectrum of the mixed crystal shows bands attributable to both DPA and MNA. The mixed DPA:MNA

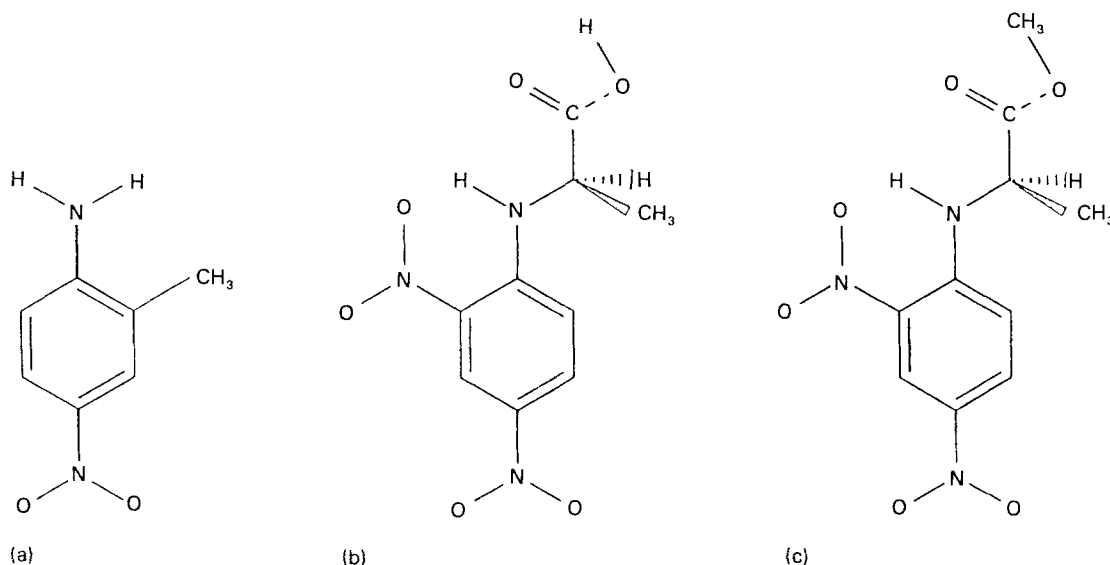


Figure 7 The chemical structures of (a) MNA, (b) DPA and (c) MAP.

crystals melt at 138(0.5) °C, which lies between that of MNA (133(1) °C) and DPA (169(2) °C) and the specific heat of the mixed crystal is observed to be lower than that of MNA. The specific heat of the complex (25.3(4) cal g<sup>-1</sup>) lies between those of DPA (20.5(5) cal g<sup>-1</sup>) and MNA (37.2(2) cal g<sup>-1</sup>).

In the absence of the optical absorption spectrum of DPA:MNA, it is difficult to explain the observed SHG efficiency. However, judging from the orange–yellow coloration of the crystals, which is similar to that of MAP:MNA [10], one might conclude that there is a likelihood of an absorption at 532 nm which may be influencing the SHG efficiency as in the case of MAP:MNA [10].

## 5. Conclusion

Large crystals of MNA were grown from solutions containing DPA as the triclinic polymorph. XRD results show that DPA does not enter the crystal structure but it may be present as an impurity. The powder efficiency of the polymorph MNA(T) is the same as that of MNA(M). Mixed DPA:MNA crystals were also grown which are orange–yellow in colour. The Raman spectrum of DPA:MNA consists of bands from both DPA and MNA, and its SHG efficiency is about the same as that of MAP.

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