New crystalline modification of terephthalic acid

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Abstract

The new crystalline modification of terephthalic acid can be obtained either from the commercially available triclinic modification by heating at 250°C or directly by a thermal hydrolysis of *p*-dicyanobenzene. It crystallises in a monoclinic system, space group $C2/m$ with $a = 8.940(2)$, $b = 10.442(2)$, $c = 3.790(1)$ Å, $V = 353.7(2)$ Å^3, $\beta = 91.21(3)°$ and $Z = 2$. Both carboxyl groups of terephthalic acid are coplanar with the phenyl ring. The molecules in the crystal are linked through the hydrogen bonds in the carboxyl groups into infinite chains. The orientational disorder is observed in the carboxyl groups. The structure of the monoclinic form is compared with the structure of both the triclinic modifications. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords*: Terephthalic acid; Powder diffraction; Crystal structure; Polymorphism; Phase transition

1. Introduction

Terephthalic acid $C_6H_4(COOH)_2$ (abbreviated as TPA) is the main starting material for the synthesis of polyethylene terephthalate (PET) which is used in the plastics manufacturing industry [1]. Commercially it is produced by the catalytic air oxidation of para-xylene [1,2]. According to Bailey and Brown [3] TPA exists in two crystalline modifications (forms I and II). Both modifications crystallise in the centrosymmetric space group of the triclinic system, with one molecule per unit cell. In both forms the molecules are linked together by hydrogen-bonded carboxyl dimers into infinite chains, forming two-dimensional layers. The main difference between these triclinic forms can be found in the mutual arrangement of the chains. Bailey

and Brown [3] obtained both forms of TPA by recrystallization of pure acid from a water solution in a glass tube at about 150°C. They stated that form I is more stable at room temperature than form II as it has a higher density. Additionally they suggested that the form II is a high-temperature modification. The phase II crystallises with a different habit (parallelepipeds) in comparison to form I (plates and needles). The drastic change in the crystal habit of TPA at temperatures above 150°C observed by Gaines and Myerson [4] was attributed to the phase transition of the high-temperature phase II. Gerasimov et al., [5] Colombo et al. [6] and Fjaer and Samuelsen [7] recognise both the triclinic forms of TPA in their Raman spectroscopic studies. However, Saska and Myerson [1,8] using the powder X-ray diffraction technique based on a wide range of TPA samples obtained under different conditions have not obtained any evidence for the presence of form II. In turn Davey et al. [9] using the scanning electron microscope (SEM)

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- - monoclinic phase

* - triclinic phase I
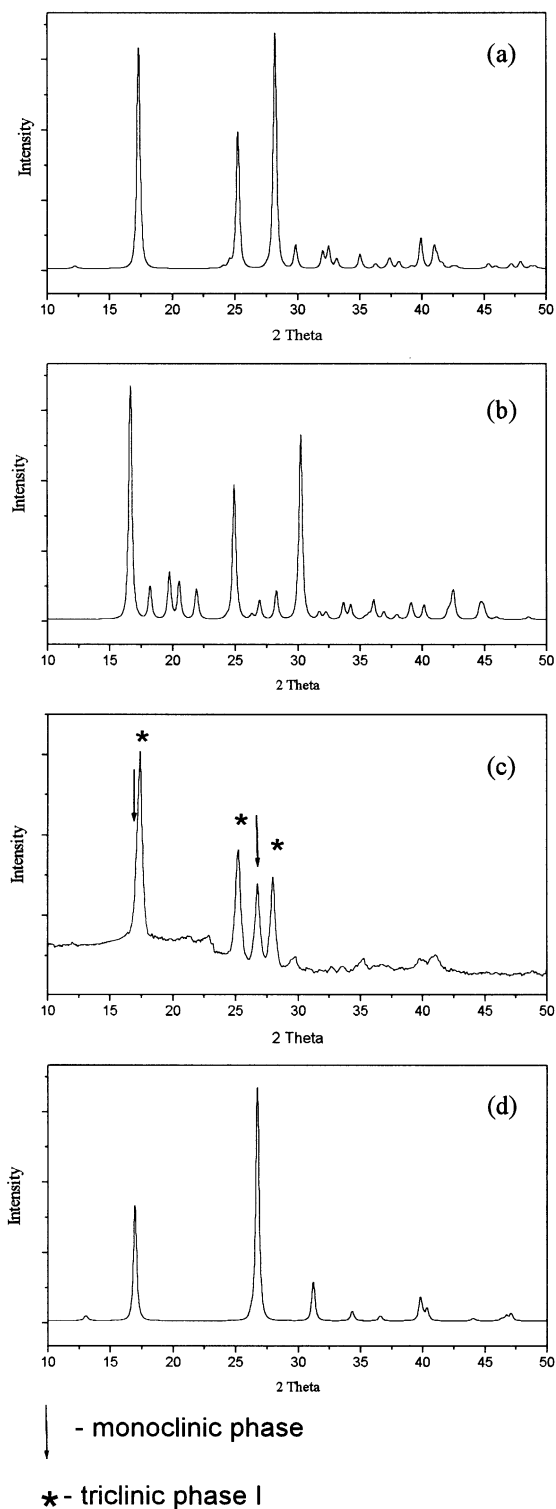
observed both the triclinic forms of TPA. Nevertheless, in contrast to the suggestions given by Bailey and Brown [3], they stated that form II is more stable at room temperature and normal pressure than form I. Additionally they suggested that form I at room temperature is the metastable modification, which is stabilised by twinning. Domenicano et al. [10] obtained the triclinic modification of TPA and they stated that it is "apparently different from either of the two forms described by Bailey and Brown" [3]. However, the powder diffraction pattern calculated for this modification is quite same as that calculated for phase I obtained by Bailey and Brown [3].

Since the available literature data concerning the different phases and the conditions of the phase transition in the TPA are inconsistent, we therefore attempted to determine the conditions in which the appropriate phases of TPA exists. As a result of our investigations a new modification of TPA in a crystalline form (monoclinic) has been obtained. In this contribution we describe the formation conditions and the crystal structure of the new monoclinic form of TPA. Additionally, the correlation between the crystal structures of the monoclinic and triclinic forms is discussed.

2. Experimental

2.1. Powder diffraction

The commercial TPA (triclinic form I) was used in the powder diffraction experiment. The several samples of TPA were heated at different temperatures in the range of 100–250°C in sealed glass ampoules for 5 h and then cooled to the room temperature. Next, their X-ray powder diffraction diagrams were taken on a STOE transmission powder diffractometer equipped with a position sensitive detector (PSD) and monochromatic CuKα_1 radiation ($\lambda = 1.540562$ Å). The powder diffraction diagrams for both the triclinic forms of TPA were calculated on

Fig. 1. X-ray powder diffraction diagrams of the terephthalic acid: (a, b) the calculated diagrams for the triclinic forms I and II, respectively; (c) experimental diagram for the sample heated at 250°; and (d) the calculated diagram for the monoclinic form.
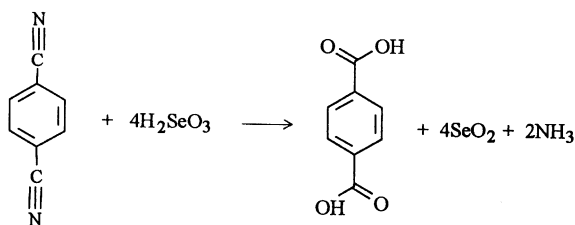
Scheme 1.

the basis of the X-ray single-crystal data [3]. The powder diffraction diagram for the monoclinic form was calculated on the basis of the present single crystal structure. All the diagrams are shown in Fig. 1.

2.2. Preparation

The crystals of the monoclinic form of terephthalic acid were prepared by a thermal hydrolysis of 1,4-dicyanobenzene according to the equation outlined in Scheme 1.

The 1,4-dicyanobenzene and H_2SeO_3 used in a molar proportion of 1:4 were mixed together and

Table 1
Crystallographic data and final refinement parameters for monoclinic form of terephthalic acid

Chemical formula	$C_6H_4(COOH)_2$
Molecular weight	168.14
Temperature (K)	295
Space group	*C2/m*
Unit cell dimensions	
a (Å)	8.940(2)
b (Å)	10.442(2)
c (Å)	3.790(1)
Vol. *V* (Å^3)	353.72(14)
Z	2
$D_{obs.}$ [a]	1.57
$D_{calc.}$	1.579
Radiation, MoKα (Å)	0.71073
Abs. Coefficient, μ (mm^{-1})	0.128
Face-indexed anal. Abs. correction, $T_{min.}$, T_{max}	0.953, 0.975
$R\,[F^2 > 2\sigma(F^2)]$ [b]	0.0254
$wR(F^2)$ [b]	0.0318
S	1.029
$\Delta\rho_{max.}/\Delta\rho_{min.}$ (eÅ^{-3})	+ 0.091, −0.092

[a] Measured by floatation.
[b] $R = \sum\|F_o| - |F_c\|/\sum F_o$, $wR = \{\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4\}^{1/2}$.
$w^{-1} = \sigma^2(F_o^2) + (0.0001P)^2 + 0.0334P$, where $P = (F_o^2 + 2F_c^2)/3$.

pressed into a pellet. The pellet ($\sim$0.5 g) was inserted into an evacuated glass ampoule and heated at 250°C for 5 h and the ampoule was then cooled in the temperature gradient. In the cooler part of the ampoule the crystals of monoclinic form of terephthalic acid as a result of sublimation are grown.

2.3. X-ray data collection

A colourless single crystal of $C_6H_4(COOH)_2$ with approximate dimensions $0.38 \times 0.30 \times 0.20$ mm^3 was used for data collection on a four-circle KUMA KM-4 diffractometer equipped with a graphite monochromator and MoKα radiation ($\lambda = 0.71073$ Å). The lattice parameters were refined by least-squares fit of 26 reflections measured in the 2ϑ range of 16–26°. A total of 928 reflections was measured in the range of $4 \leq 2\vartheta \leq 58°$ using the $\omega - 2\vartheta$ scan technique. Three standard reflections were monitored at every 50 and they showed no intensity variations. Intensities and their standard deviations were corrected for Lorenz and polarisation effects using a KUMA KM-4 software [11]. Face indexed analytical absorption was calculated using the SHELXTL program [12]. Four hundred and sixty-seven independent reflections were used for crystal structure solution and refinement.

2.4. Structure solution and refinement

The structure was solved using the SHELX97 program [12]. The direct methods gave the positions of carbon and oxygen atoms. The hydrogen atoms in the ring were located from the difference Fourier synthesis. The positions of the hydrogen atoms in the phenyl ring were refined, but their isotropic thermal parameters were fixed as $1,2U_{eq}$ of the carbon atom linked directly to the H-atom. As the C−O bond lengths in the carboxyl groups are symmetrically equivalent (space group *C2/m*) the hydrogen atoms of the COOH groups should be disordered. In the final refinement (based on F^2), the hydrogen atom of carboxyl group was included with the occupation factor of 0.5. The final unweighted and weighted agreement factors converged to $R[F^2] = 0.0254$ and $wR = 0.0318$, a goodness-of-fit calculation resulted in a value of 1.029 at the final convergence. The final difference Fourier synthesis showed no peaks of chemical significance, the largest was +0.091 and −0.092 eÅ^{-3}. Scattering factors for neutral atoms

Table 2
Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i a_j \mathbf{a}_i \mathbf{a}_j$)

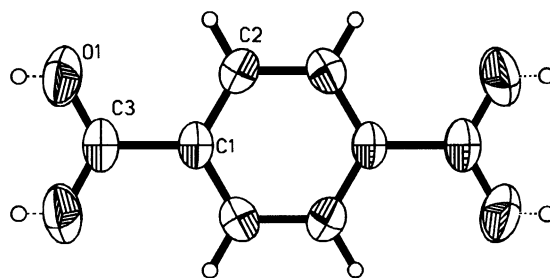| Atom	x	y	z	U_{ij}
O1	0.3595(1)	0.39529(7)	0.3652(2)	0.0896(3)
C1	0.1429(1)	0.5	0.1435(3)	0.0448(3)
C2	0.0718(1)	0.38653(8)	0.0719(2)	0.0556(2)
C3	0.2974(1)	0.5	0.3013(3)	0.0538(3)

Fig. 2. Molecular structure of terephthalic acid with numbering of the atoms. The H atoms of the carboxyl groups are disordered with the occupation factor of 0.5.

and the correction for anomalous dispersion were as given in the SHELX97 program [13]. Final agreement factors, details of data collection and crystallographic data are listed in Table 1. Final atomic co-ordinates and equivalent isotropic displacement parameters are given in Table 2. Bond lengths and angles are listed in Table 3.

3. Results and discussion

In the course of the heating process of several samples of TPA in an evacuated glass ampoule we have stated, on the basis of the X-ray powder diffraction technique, that in all the samples heated below 250°C only the triclinic form I is present. Thus the triclinic form I is stable in the said conditions. Our observations are consistent with those described by Saska and Myerson [1,7]. The powder diffraction diagram taken for the sample heated at 250°C is more complicated (Fig. 1), because besides the powder diffraction lines, which belong to the triclinic form I, additional lines are also observed. As can be seen from Fig. 1 these new lines do not correspond to the triclinic phase II. Since we have not observed any evidence on the decomposition of TPA at the condi-

Table 3
Bond lengths (Å) and angles (°)

O1–C3	1.248(1)	C1–C2	1.369(1)
C1–C3	1.493(2)	C1–C2[a]	1.369(1)
C2–C2[b]	1.384(2)		
O1–C3–O1[a]	122.4(1)	O1–C3–C1	118.8(1)
C1–C2–C2[b]	120.1(1)	C2–C1–C3	120.1(1)
C2–C1–C2[a]	119.9(1)	C2[a]–C1–C3	120.1(1)

[a] Symmetry code: x, $1 - y$, z
[b] Symmetry code: $-x$, y, $-z$

tions applied, we therefore suppose that the additional lines observed at the powder diffraction pattern belong to the new, unknown up to now, modification of TPA. Unfortunately we have not been able to obtain the pure phase of the new TPA modification by the method mentioned above (even at higher temperatures and/or longer heating times). Thus, both phases (triclinic form I and a new phase) co-exist at the conditions applied above (at a temperature of 250°C). In order to obtain the pure phase of a new modification of TPA we decided to carry out the synthesis of TPA by a thermal hydrolysis of 1,4-dicyanobenzene at a temperature at which this modification has been observed. The thermal hydrolysis of 1,4-dicyanobenzene leads to the formation of good quality single crystals of TPA, which in fact appeared to be the new phase obtained by the former procedure. The prominent lines observed on the powder diffraction diagram calculated on the basis of the X-ray single crystal data described below (Fig. 1d) are consistent with those observed at the powder diffraction diagram taken for the samples heated at 250°C (Fig. 1c).

The crystal of monoclinic form of TPA is built up of hydrogen-bonded chains. This structural motif is typical for the crystal structures of dicarboxylic acids. The phenyl ring of TPA molecule is closely planar, but not perfectly hexagonal. This distortion can be attributed to the substitution effect of the carboxyl groups. Both carboxyl groups of the TPA molecule in the monoclinic modification are coplanar with the phenyl ring (Fig. 2). Similar orientation of both carboxyl groups in relation to the phenyl ring can be found in the triclinic form II, but different in the
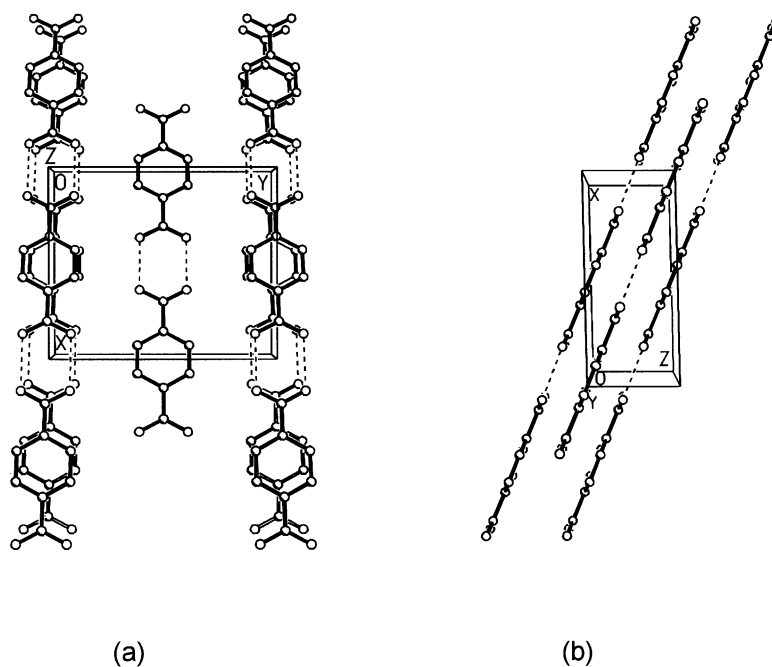
Fig. 3. Molecular arrangement of terephthalic acid in the crystal shows the hydrogen-bonded chains: (001) projection (a); and (010) projection (b).

triclinic form I wherein the carboxyl groups are inclined by $\pm 5.25°$ [3]. In the monoclinic form, akin to the crystals of the triclinic forms, a orientational disorder in carboxyl groups is observed. The positions of the acidic hydrogen atoms as well as the single and double carbon–oxygen bonds are found to be averaged (both C–O bonds have a distance of 1.248(1) Å). According to the neutron diffraction [14], neutron scattering [15] and NMR [16] studies on the terephthalic acid it can be concluded that the disorder is of a dynamic origin caused by the double proton exchange associated with an asymmetric double minimum potential. The disordered hydrogen atom of the carboxyl group forms two symmetrically equivalent hydrogen bonds with $O\cdots O$ distance of 2.691(2) Å. They are slightly weaker than those observed in the triclinic form I (with $O\cdots O$ distance of 2.608 Å) [3].

The hydrogen-bonded chains in the monoclinic form of TPA are parallel to [101] direction and form layers parallel to $(10\bar{1})$ plane as shown in Fig. 3. In one layer, as in the triclinic form II, the benzene rings

of one chain are adjacent to the benzene rings of the neighbouring chain. This is in contrast to the triclinic form I where the chains in one layer are shifted in such a way that the benzene rings are adjacent to the carboxyl dimers of the neighbouring chain. The neighbouring layers in monoclinic modification of TPA are separated by $c/2$ while in both the triclinic forms the layers are separated by c. Additionally in the monoclinic modification the chains of the neighbouring layers are shifted by $a/2$ and $b/2$ whereas in both the triclinic forms the chains of one layer lie above the chains of the neighbouring layer.

4. Supplementary material

Additional materials comprising atomic coordinates, anisotropic thermal parameters, full bond length and angles for terephthalic acid have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC 154875.

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