CHAPTER 2

NEW POLYMORPH OF 1,3,5–TRIAZINE–2,4,6–TRIAMINEHEXAACETIC ACID

From the perspective of supramolecular chemistry, derivatives of 1,3,5–triazine, which are apt to involve in various non–covalent bonds in addition to an excellent capability to coordinate to metals, are regarded as some of the most remarkable molecular synthons for a design of new compounds [1, 2]. Examples of the fabrication of intricate frameworks expressing different dimensionalities in the presence of these exquisite molecules as organic templates are also continuously increasing; *e.g.* three–dimensional $\{H_2[Zn_6(\mu_4\text{–}O)(TATB)_4]\}_n$, $[Cd_3(TATB)_2]_n$, and $[Mn_3(TATB)_2]_n$ where H_3TATB = 4′,4″–*S*–triazine–2,4,6–triyltribenzoic acid [3], two–dimensional $[Ag(L)_2](ClO_4)$ and $[Ag(L)_2](CF_3SO_3)$ where L = 2,4,6–trimethoxy–1,3,5–triazine [4], zero–dimensional $LnL_3(TPTZ)$ where Ln = Eu, Tb, Er and TPTZ = 2,4,6–tri(2–pyridyl)–1,3,5–triazine [5]. Among the reported 1,3,5–triazine derivatives, 1,3,5–triazine–2,4,6–triaminehexaacetic acid (TTHA) can be of great benefit for crystal engineering due to its highly symmetrical and flexible structure with multitopic ligating potential. Crystal growth of TTHA from aqueous solution was formerly reported [6]. The compound crystallized in the monoclinic space group $C2/c$ with the unit cell parameters a = 5.057(1) Å, b = 21.607(2) Å, c = 17.406(2) Å, β = 91.69(1)°, V = 1900.0(0) Å^3, Z = 4. The architecture of the structure was characterized by the stacking of puckered molecular sheets which in turn resulted in channels of various sizes. The assembly of TTHA was crystallographically shown to be principally supported by the O−H···O type of hydrogen bonding interactions. Significance of non−covalent interactions including hydrogen bonding in directing the assemblage of molecules has been well acknowledged and employed contemplatively in crystal engineering [7]. In a similar manner, unprecedented polymorphs of both known and unknown compounds have been designed and discovered [8–10].

Herein, the crystal structure of a new polymorph of TTHA is reported and discussed with reference to the previously reported structure. Influences of hydrogen bonding interactions in the formation of the new polymorph are described. The Fourier transform infrared (FT−IR) and UV–Vis spectroscopic results are included. Although the molecular structure of the reported crystal is closely similar to the structure reported earlier [6], details on molecular conformation and supramolecular arrangement are however significantly different. The reported structure which will be denoted as **TTHA−II** hereafter can therefore be regarded as a new polymorph of the formerly reported TTHA, denoted as **TTHA−I**.

2.1 Experimental

2.1.1 Microwave−assisted crystal growth of TTHA−II

In the attempt to prepare new polyoxovanadate frameworks by microwave−assisted hydrothermal process in the presence of TTHA as an organic template, crystals of the organic molecule were growth fortuitously. In one typical experiment, the reaction mixture was prepared from an aqueous solution of oxovanadium(IV) ions, prepared in priori from 0.15 mol·dm^{-3} ammonium metavanadate (NH_4VO_3; AJAX, 99.5%) [11], and 0.050 mol·dm^{-3} TTHA which was synthesized by W. Karuehanon *et al.* according to the method described in the literature [12]. The crystals of the organic molecule were grown in the reaction conducted in a closed Teflon container under autogenous pressure generated using microwave irradiation at 630 W for 1 hour (Whirlpool XT–25ES/S, 900 W, 2.45 GHz). The filling capacity of the reaction was *ca.* 70%. After the microwave was switched off, the reaction was left undisturbed until it was cooled down to room temperature, at which the crystals were separated from the bulk synthesized product under an optical microscope.

2.1.2 Structure determination and refinement

Data of 6,227 independent reflections were collected at 296(2) *K* in a range of 2.3° $\leq \theta \leq$ 26.34° on 0.60 × 0.20 × 0.16 mm^3 TTHA single crystal, using X8 APEX II Bruker diffractometer and APEX II software [13]. Absorption collection was applied using SADABS [14]. The data were then reduced and refined resulting in 1,882 unique reflections and 1,157 reflections with $I > 2\sigma(I)$ [15]. The structure was determined by direct methods using SHELXS–97 [16] *via* WinGX interface [17]. All non–hydrogen atoms were refined anisotropically by full matrix least–squares on F^2 using SHELXL–97 [16]. The hydrogen atoms were placed in their calculated positions and refined using the riding model. Although the value of R_{int} of the collected data was rather high, *i.e.* 0.155, the structure could be successfully solved and refined with reasonable $R[I > 2\sigma(I)]$ and excellent goodness of fit; $C2/c$, a =

20.443(4) Å, *b* = 10.5104(14) Å, *c* = 9.8022(11) Å, β = 118.212(6)°, *V* = 1855.9(5) Å^3, *Z* = 4, *R* = 0.112, *Rw* = 0.273 and *S* = 1.038. Crystallographic data and summary on structure determination are listed in Table 2.1. Selected bond lengths and angles are listed in Table 2.2.

2.1.3 Vibrational and electronic spectroscopic study of TTHA–II

The FT–IR spectrum of **TTHA–II** was recorded on the ground crystals prepared as a KBr disc, using FT–IR Bruker TENSOR 27 (Germany). The UV–Vis spectrum was collected on the suspension of 0.10 g of ground crystals in 1.00 cm^3 methyl alcohol, using UV–Vis spectrophotometer (Perkin Elmer, Lambda25, USA).

Table 2.1 Crystal and experimental data for **TTHA–I** and **TTHA–II**.

Identification code	**TTHA–I** [6]	**TTHA–II**
Molecular formula	$C_{15}H_{18}O_{12}N_6$	$C_{15}H_{18}O_{12}N_6$
Formula weight	474.3	474.35
Space group	*C2/c*	*C2/c*
a (Å)	5.057(1)	20.443(4)
b (Å)	21.607(2)	10.5104(14)
c (Å)	17.406(2)	9.8022(11)
β (°)	91.69(1)	118.212(6)
V (Å^3)	1900.0(0)	1855.9(5)
Z	4	4
T (K)	130	296(2)
$\rho_{calc.}$ (g·cm^{-3})	1.797	1.698
μ (Mo–*K*α, mm^{-1})	0.07	0.15
R, *Rw* ($I > 2\sigma(I)$)	0.0464, 0.1267	0.1117, 0.2380
Goodness of fit	1.162	1.038

Table 2.2 Selected geometric parameters for **TTHA–II**.

Bond distances (Å)			
N1–C6	1.345(8)	N3–C4	1.448(6)
N1–C1	1.451(6)	N3–C5	1.371(6)
C1–C2	1.512(7)	N3–C7	1.464(6)
C2–O21	1.213(6)	N4–C5	1.337(6)
C2–O22	1.305(6)	N4–C6	1.342(5)
N2–C5	1.331(5)	C7–C8	1.518(6)
C3–O31	1.222(5)	C8–O81	1.215(6)
C3–O32	1.301(6)	C8–O82	1.309(6)
C3–C4	1.504(6)		
Bond angles (°)			
C6–N1–C1	121.0(3)	N2–C5–N4	126.8(4)
N1–C1–C2	113.6(4)	N2–C5–N3	115.9(4)
O21–C2–O22	121.4(5)	N4–C5–N3	117.3(4)
O21–C2–C1	123.1(4)	N3–C7–C8	114.2(4)
O22–C2–C1	115.5(4)	N4–C6–N1	117.0(3)
O31–C3–O32	122.9(4)	O81–C8–O82	119.4(4)
O31–C3–C4	123.1(4)	O81–C8–C7	122.1(4)
O32–C3–C4	114.0(4)	O82–C8–C7	118.4(4)
N3–C4–C3	112.4(4)	C5–N4–C6	113.4(4)
C5–N3–C4	118.5(4)	C4–N3–C7	122.6(4)
C5–N3–C7	117.3(4)		

2.2 Results and discussion

2.2.1 Crystal structure and hydrogen bonding network analysis of TTHA–II

At first glance, molecular structure of **TTHA–II** is closely similar to that of **TTHA–I**. The asymmetric unit contains only a fraction of molecule which is completed by the operation about the two–fold rotation axis transiting upon atoms on the Wyckoff positions 4*e* (N1, N2 and C6 in **TTHA–II**, Fig. 2.1). Relatively large thermal parameters of the terminal O atoms observed in **TTHA–II** should be due to the inherent flexibility of the –CH_2COOH pendants, compared to the strained core structure of the molecule. Bond distances for the N–C bonds of the core triazine and those directly attached to it (1.331(5)–1.342(5) Å) are expectedly shorter than the C–N bond distances found for the –$N(CH_2COOH)_2$ residues (1.448(6)–1.464(6) Å). This is in good accordance with the extensive electron delocalization of the aromatic triazine core. Differences in bond distances between the unsaturated (1.213(6)–1.222(5) Å) and the saturated (1.301(6)–1.309(5) Å) bonds are distinct and in excellent consistence with ranges of values reported to the Cambridge Structure Database [18]. Discrimination in orientations of the –CH_2COOH pendants of the two polymorphs can therefore be ascertained. It may be noted after all that the hydrogen atoms have been assigned subjecting to the maximization of hydrogen bonding interactions, as shown in Fig. 2.2 and listed in Table 2.3.

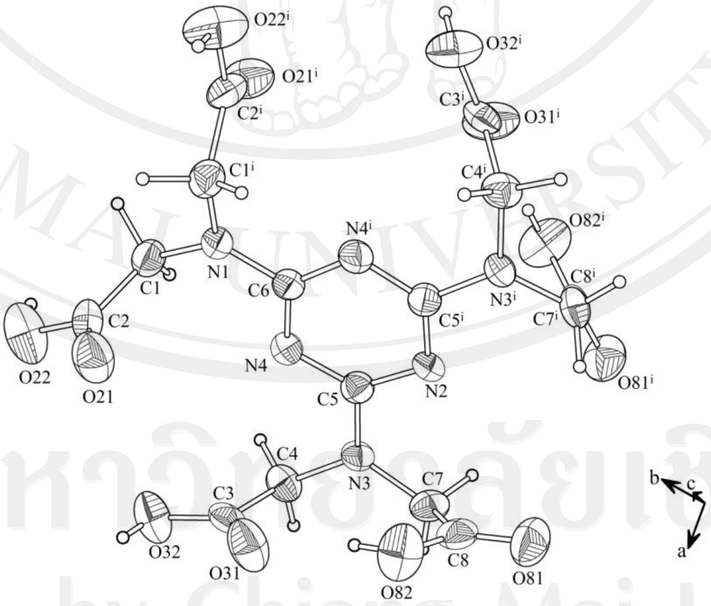

Fig. 2.1 ORTEP drawing of molecular unit in **TTHA–II** showing atom numbering scheme and 70% probably displacement ellipsoids for non–hydrogen atoms. Symmetry code: (i) - *x*, *y*, 1.5 - *z*.

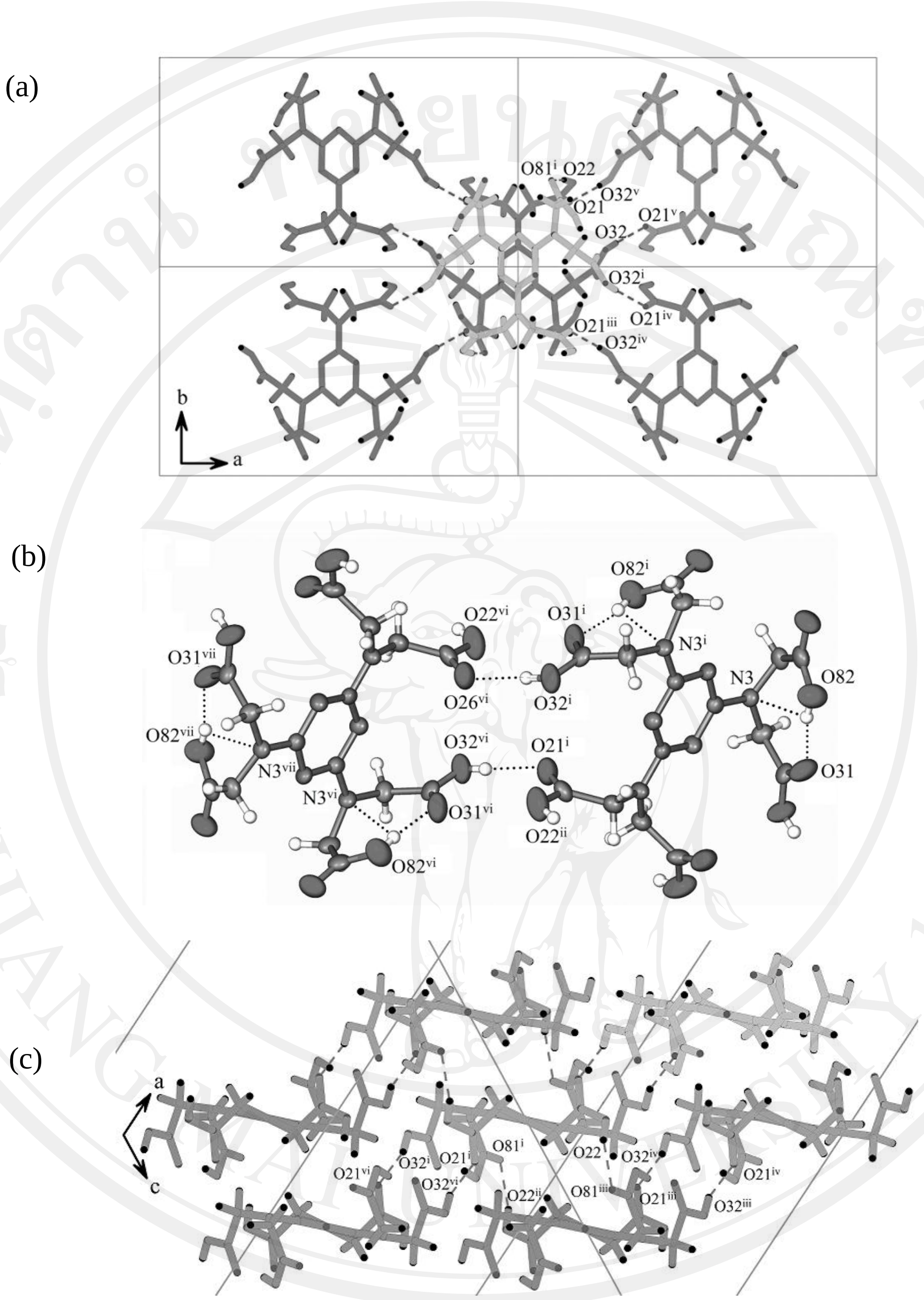

Fig. 2.2 Hydrogen bonding interactions (dotted lines) in **TTHA–II** illustrated by (a) capped stick model showing intermolecular interactions, (b) 70% thermal ellipsoids showing intramolecular interactions, and (c) capped stick model showing the packing of molecular units. Symmetry codes: (i) - *x*, *y*, 1.5 - *z*; (ii) - *x*, 2 - *y*, 2 - *z*; (iii) *x*, 2 - *y*, 0.5 + *z*; (iv) 0.5 - *x*, - 0.5 + *y*, 2.5 - *z*; (v) 0.5 - *x*, 2.5 - *y*, 2 - *z*; (vi) - 0.5 + *x*, 2.5 - *y*, - 0.5 + *z*; (vii) - 0.5 - *x*, 2.5 - *y*, 1 - *z*.

Table 2.3 Details of the hydrogen bonding interactions in **TTHA–II**. A hydrogen bond donor and acceptor are denoted as D and A, respectively.

D–H···A [a]	D–H, (Å)	H···A, (Å)	D···A, (Å)	∠ D–H···A, (°)
O22–H22···O81[i]	0.82	2.01	2.794(5)	161
O32–H32···O21[ii]	0.82	1.85	2.639(5)	160
O82–H82···O31	0.82	1.77	2.570(5)	165
O82–H82···N3	0.82	2.43	2.851(5)	113

[a] Symmetry codes:(i) x, $2 - y$, $0.5 + z$; (ii) $0.5 - x$, $2.5 - y$, $2 - z$.

Despite close similarity in molecular structure of the two polymorphs, spatial arrangement of the flexible residues of the molecules are different. In **TTHA–I**, the conformation of the –N(CH$_2$COOH)$_2$ residues was reportedly adjusted in order to fully facilitate the formation of intermolecular hydrogen bonds [6]. There was no report on the presence of any intramolecular interaction. In **TTHA–II**, the presence of intramolecular hydrogen bonding interactions are however vivid. Regarding the intermolecular hydrogen bonding interactions, the smallest ring pattern found in **TTHA–I** is the common pattern $R_2^2(8)$ observed in the packing of polycarboxylates. This is however not the case for **TTHA–II**, of which the smallest ring is $R_2^2(24)$; O32–H32···O21 and O22–H22···O81 (Fig. 2a), which is due to the difference in relative orientations of the –CH$_2$COOH pendants. In the case of **TTHA–II**, the O atoms of two adjacent molecules (O22 and O31), which are located in a close proximity to possibly form $R_2^2(8)$ hydrogen bonding, deflect away to establish interactions with the other O atoms; O82–H82···O31 and O22–H22···O81. One of the principal consequences is the formation of intramolecular $S_1^1(8)$ hydrogen bonding interactions (O82–H82···O31 in Fig. 2b). The orientation of atom O82 as described additionally results in another intramolecular O82−H82···N3 hydrogen bonding interaction, which on the other hand secures the two $–CH_3COOH$ pendants of the same N3 anchor.

The establishment of the O22−H22···O81 interactions consequently result in the stacking of the **TTHA−II** molecules into molecular columns along *c*, as shown in Fig. 2.3. The adjacent triazine planes within the column exhibit the offset face−to−face π−stacking (Fig. 2.3a) with inter−plane distance of 3.581 Å, centroid−to−centroid distance of 4.982 Å, and an angle between the ring normal to the core triazine plane and the centroid vector of *ca.* 40° [19]. These molecular columns are plainly arranged according to the characteristic symmetries of *C*2/*c*, and transfixed by the O32−H32···O21 interactions. The structure of **TTHA−II** can therefore be viewed as the hydrogen bonded bundle of **TTHA−II** molecular columns (Fig. 2.3b), which is clearly distinct from an assembly of the puckered layers in **TTHA−I** [6]. Dissimilarity in the powder X−ray diffraction patterns simulated from the single crystal data of both polymorphs affirms distinct crystal structures of the compound, as shown in Fig. 2.4.

Although factors governing the emergence of new polymorphs and criteria in defining the existence of hydrogen bonding interactions are still controversial, the new polymorph of TTHA reported here is evidently the result of the flexibility of the $–N(CH_2COOH)_2$ residues. The involvement of every terminal $–CH_2COOH$ pendants in the formation of hydrogen bonds, which in turn results in new supramolecular organization in **TTHA−II**, illustrates the significant role of hydrogen bonding in regulating the crystal structure. Experimental factor determining different hydrogen bonding patterns and supramolecular packing between **TTHA–I** and **TTHA–II** is yet inconclusive. It may be due to the application of microwave irradiation, the data collection temperature, or the presence of other species during the synthesis. A thorough experimental study will be demanded before a conclusion can be made.

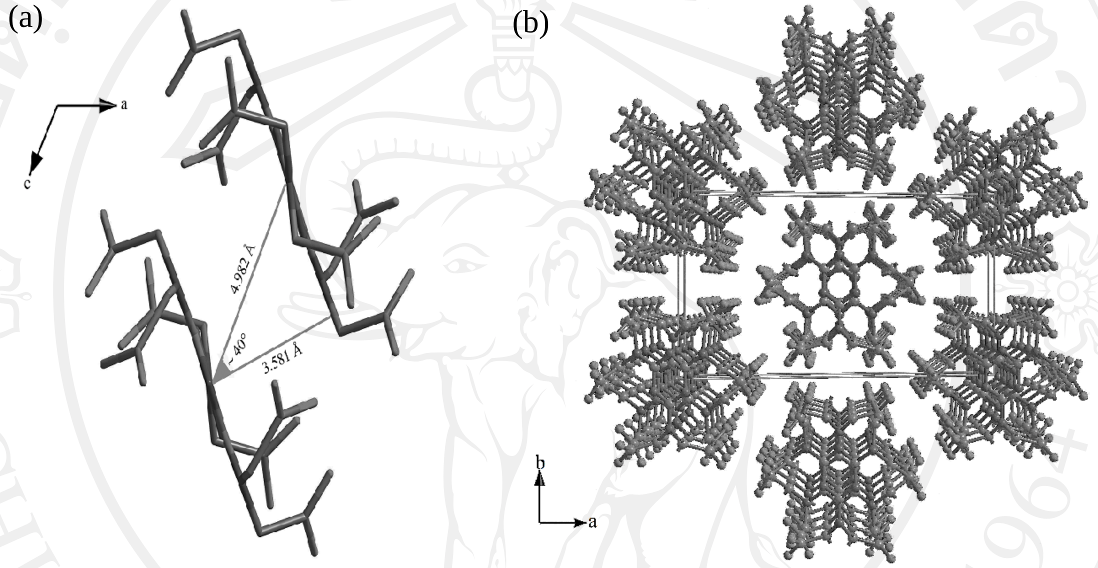

Fig. 2.3 Crystal packing in **TTHA–II** showing (a) face–to–face π–stacking and (b) molecular columns built up from the stacking of the molecules in *c*–direction.

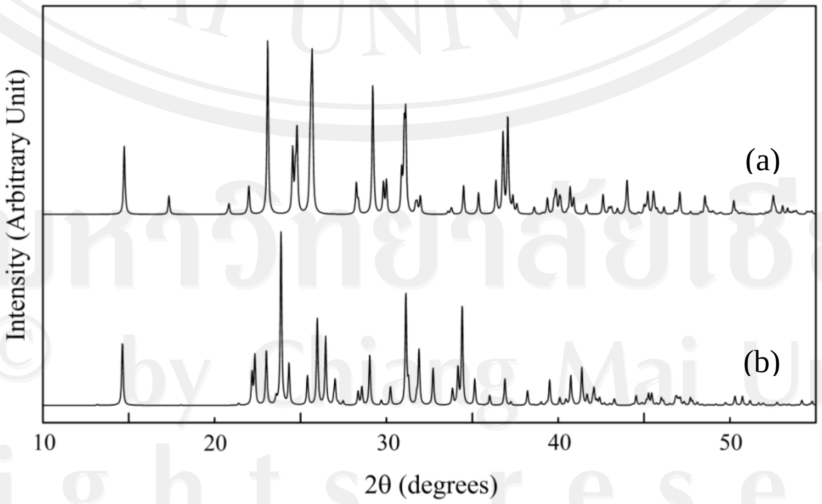

Fig. 2.4 Simulated X–ray diffraction patterns of (a) **TTHA–I** and (b) **TTHA–II**.

2.2.2 Spectroscopic study of TTHA–II

The FT–IR spectrum collected on the ground **TTHA–II** crystals is shown in Fig. 2.5. The hydrogen bonded O–H of the $–CH_2COOH$ chains are revealed by characteristic broad and intense absorption in the range 3690–3150 cm^{-1} and another broad and weak band centering at 2522 cm^{-1} [20]. The out–of–phase and the in–phase CH_2 stretch occur at 2980 and 2940 cm^{-1}, respectively. Intense bands located at 1722 and 1232 cm^{-1} are typical feature of the carbonyl group in carboxylic acid while the most intense feature at 1552 cm^{-1} is corresponded to the in-phase stretch of the resonated C–N bonds exogenous to the triazine ring [21]. The UV–Vis spectrum collected on the **TTHA–II** suspension in methyl alcohol (Fig. 2.6) exhibit the intense absorption peak at 225 nm attributing to the characteristic $n\rightarrow\pi^*$ transition which is commonly found for the triazine derivatives, while two small features at 275 and 315 nm are associated with $\pi\rightarrow\pi^*$ transition of the core triazine [22].

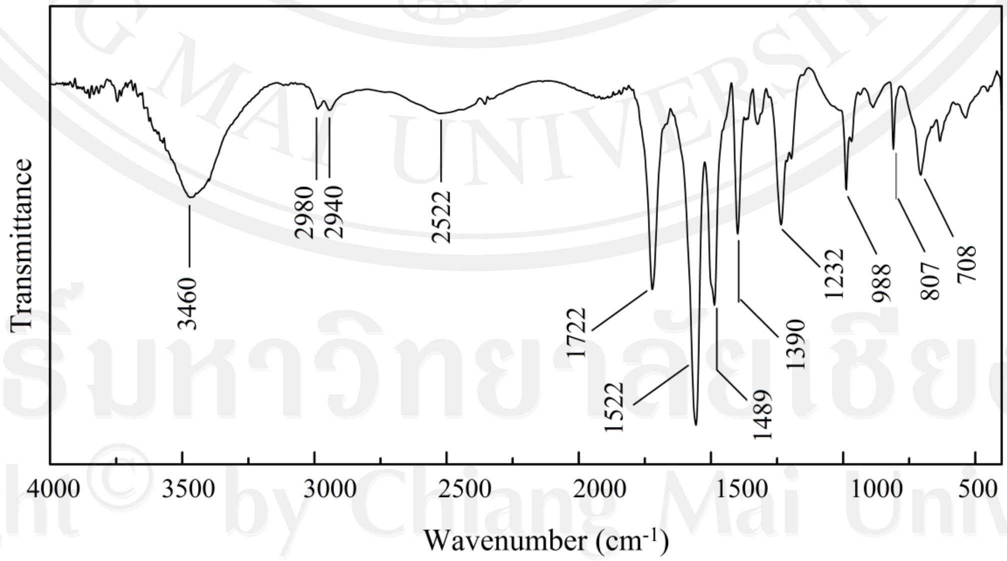

Fig. 2.5 FT–IR spectrum collected on the ground crystals of **TTHA–II**.

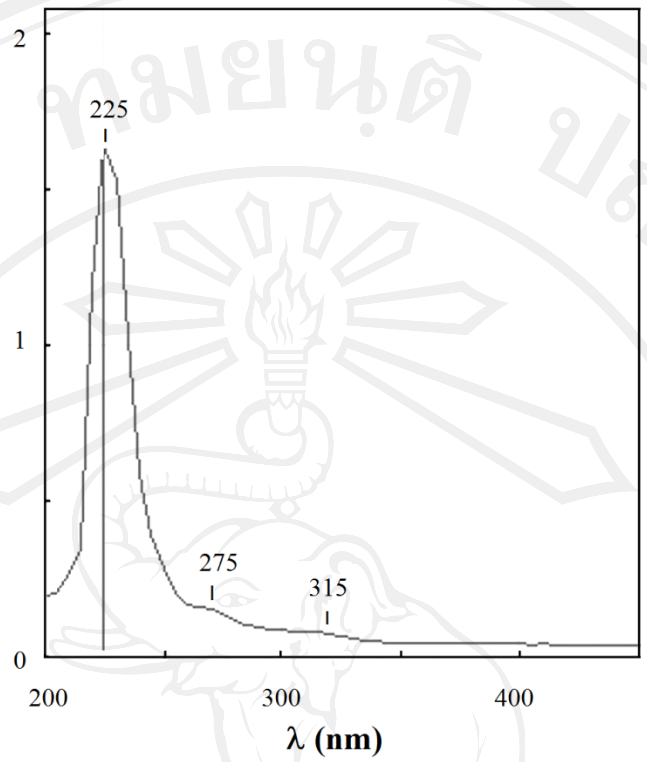

Fig. 2.6 UV−Vis spectrum collected on a suspension of the ground **TTHA–II** crystals in methyl alcohol.

2.3 Conclusions

Single crystal of **TTHA–II**, a new polymorph of **TTHA–I**, has been growth by the microwave–assisted hydrothermal synthesis. The principal feature of the new polymorph **TTHA–II** is characterized by a bundle of molecular columns each of which is built up of molecular units stacked along *c* in the offset face−to−face manner. Significance of hydrogen bonding interactions in regulating the assembly of molecules in the structure is then demonstrated. Detailed differences in molecular conformation, type and pattern of hydrogen bonding interactions are discussed and distinguished from the previous polymorph. The vibrational and electronic spectroscopic studies are included.

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