Journal of Molecular Structure 1006 (2011) 128–135

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Salt and co-crystal formation from 2-(imidazol-1-yl)-1-phenylethanone and different acidic components

Shouwen Jin [a,*], Ming Guo [b], Daqi Wang [c], Han Cui [a]

[a] Tianmu College of ZheJiang A & F University, Lin'An 311300, PR China
[b] Graduate Department ZheJiang A & F University, Lin'An 311300, PR China
[c] Department of Chemistry, Liaocheng University, Liaocheng 252059, PR China

ARTICLE INFO

Article history:
Received 9 June 2011
Received in revised form 30 August 2011
Accepted 30 August 2011
Available online 7 September 2011

Keywords:
Crystal structure
Hydrogen bonds
Secondary interactions
2-(Imidazol-1-yl)-1-phenylethanone
Acidic components

ABSTRACT

Four crystalline adducts derived from 2-(imidazol-1-yl)-1-phenylethanone and the acidic compounds (2,4,6-trinitrophenol, p-nitrobenzoic acid, m-nitrobenzoic acid, and 5-nitrosalicylic acid) were prepared and characterized by X-ray diffraction analysis, infrared spectrum, melting point, and elemental analysis. All supramolecular architectures of **1**–**4** involve extensive classical hydrogen bonds as well as other noncovalent interactions. The results presented herein indicate that the strength and directionality of the N—H···O, O—H···N, and O—H···O hydrogen bonds (ionic or neutral) between acidic components and 2-(imidazol-1-yl)-1-phenylethanone are sufficient to bring about the formation of binary organic acid–base adducts.

1. Introduction

Supramolecular interactions have attracted considerable attention during the past few years because the utilization of intermolecular noncovalent interactions is relied upon for the design and development of functional materials [1]. Noncovalent interactions form the backbone of supramolecular chemistry and include classical/nonclassical hydrogen bond, stacking, electrostatic, hydrophobic and charge-transfer interactions [2]. Of these interactions hydrogen bond interactions are well-established supramolecular interactions and there have been many reported topology structures assembled through hydrogen bonds, such as an infinite 1-D chain [3], 1-D tapes [4], 2D sheet [5], and 3-D networks [6].

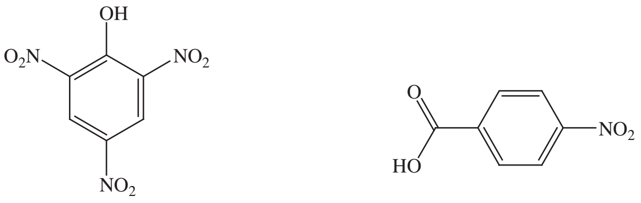
Because of the predictable supramolecular properties and the ability to form strong hydrogen bonds, carboxylic acids were frequently chosen as building blocks for crystal engineering [7–9]. Numerous heterodimers composed of carboxylic acids and a variety of N-containing basic building blocks have been documented recently [10–14]. Hydrogen bonding between hydroxyl groups of carboxylic acids and heterocyclic nitrogen atoms has been proved to be a useful and powerful organizing force for the formation of supramolecules. It should be noted that these structures are normally held together by hydrogen bonding, and in this regard, the most frequently used moieties with hydrogen bonding capability are pyridyl and carboxyl. Recently, another building block that has become quite popular is imidazole or its derivatives, owing to their assembling capacity via acid–base recognition with a large number of molecules possessing acidic sites, especially carboxylic acids [15–27].

In addition to an imidazole group, 2-(imidazol-1-yl)-1-phenylethanone bears a C═O group and a benzene ring. The carbonyl group is a good acceptor in forming noncovalent interactions, and the benzene moiety may give aromatic stacking interactions, thus carrying out the binary adducts between the acidic compounds and 2-(imidazol-1-yl)-1-phenylethanone may display the different non-bonding ability of the three different functional groups. Following our previous works of acid–base adducts based on imidazole derivatives and carboxylic acids [28–30], we herein report the synthesis and crystal structure of four supramolecular assemblies assembled through hydrogen bonding interactions between acidic tectons and 2-(imidazol-1-yl)-1-phenylethanone. In this study, we obtained four organic acid–base adducts composed of acidic units and 2-(imidazol-1-yl)-1-phenylethanone (Scheme 1), namely 2-(imidazol-1-yl)-1-phenylethanone: (2,4,6-trinitrophenol) (**1**) [$(HL)^+ \cdot (pic^-)$, pic^- = picrate, L = 2-(imidazol-1-yl)-1-phenylethanone], 2-(imidazol-1-yl)-1-phenylethanone: (p-nitrobenzoic acid) (**2**) [$(HL)^+ \cdot (L) \cdot (Hnba) \cdot (nba)^-$, Hnba = p-nitrobenz oic acid], 2-(imidazol-1-yl)-1-phenylethanone: (m-nitrobenzoic acid) (**3**) [(L · Hmba), Hmba = m-nitrobenzoic acid], and 2-(imidazol-1-yl)-1-phenylethanone: (5-nitrosalicylic acid) (**4**) [$(HL) \cdot (5\text{-nsa}^-)$, 5-nsa^- = 5-nitrosalicylate].

---

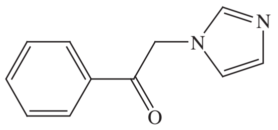
* Corresponding author. Tel./fax: +86 571 6374 6755.
E-mail address: jinsw@zafu.edu.cn (S. Jin).

0022-2860/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2011.08.058



2,4,6-trinitrophenol p-nitrobenzoic acid

m-nitrobenzoic acid 5-nitrosalicylic acid



2-(imidazol-1-yl)-1-phenylethanone

Scheme 1.

2. Experimental section

2.1. Materials and methods

2-(imidazol-1-yl)-1-phenylethanone (L) was prepared according to a modified procedure of the literature [31]. All other reagents were commercially available and used as received. The C, H, and N microanalysis were carried out with a Carlo Erba 1106 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in range 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Melting points were recorded on an XT-4 thermal apparatus without correction.

*2.2. Preparation of compounds **1–4***

*2.2.1. 2-(imidazol-1-yl)-1-phenylethanone: (2,4,6-trinitrophenol) [(HL)$^+$ · (pic$^-$), pic$^-$ = picrate, L = 2-(imidazol-1-yl)-1-phenylethanone], (**1**)*

2-(imidazol-1-yl)-1-phenylethanone (18.6 mg, 0.10 mmol) was dissolved in 3 mL methanol. To this solution, 2,4,6-trinitrophenol (23 mg, 0.1 mmol) in 10 ml of methanol was added. Yellow block crystals were obtained after several days by slow evaporation of the solvent (yield: 33 mg, 79.46%). mp 222–224 °C. Elemental analysis: Calc. for $C_{17}H_{13}N_5O_8$: C, 49.12; H, 3.13; N, 16.85. Found: C, 49.08; H, 3.06; N, 16.82. Infrared spectrum (cm^{-1}): 3440s(ν_{as}(NH)), 3236s(ν_s(NH)), 3194s, 3106s, 2968m, 2880m, 2826m, 2370m, 2322m, 1740m, 1697s, 1638vs(ν(C=O)), 1597m, 1525s(ν_{as}(NO$_2$)), 1480m, 1440m, 1400m, 1346m, 1324s(ν_s(NO$_2$)), 1260s, 1226m, 1156m, 1104w, 1080m, 1020m, 980m, 896m, 820m, 772m, 720m, 680m, 644m, 602m, 540m.

*2.2.2. 2-(imidazol-1-yl)-1-phenylethanone: (p-nitrobenzoic acid) [(HL)$^+$ · (L) · (Hnba) · (nba$^-$), Hnba = p-nitrobenzoic acid] (**2**)*

2-(imidazol-1-yl)-1-phenylethanone (18.6 mg, 0.10 mmol) dissolved in 1 mL ethanol. To this solution, p-nitrobenzoic acid (16.7 g, 0.1 mmol) in 6 mL of methanol was added. Colorless crystals were obtained after several days of slow evaporation of the solvent, yield: 27 mg, 76.42% (based on L). mp 198–199 °C. Elemental analysis: Calc. for $C_{36}H_{30}N_6O_{10}$: C, 61.13; H, 4.24; N, 11.88. Found: C, 61.12; H, 4.18; N, 11.82. Infrared spectrum (cm^{-1}): 3456s(multiple, ν_{as}(NH)), 3223s(ν_s(NH)), 3146m, 3064m, 2960m, 2842m, 2718m, 2498w, 2374m, 2213m, 1976w, 1902w, 1836w, 1783w, 1718s(ν(C=O)), 1644vs(ν(C=O)), 1606s(ν_{as}(COO$^-$)), 1578m, 1533s (ν_{as}(NO$_2$)), 1466w, 1374s(ν_s(COO$^-$)), 1328s(ν_s(NO$_2$)), 1280s (ν(C–O)), 1250m, 1195m, 1150w, 1102w, 1069m, 952m, 903m, 856m, 806m, 757m, 726m, 680m, 627m, 572m.

*2.2.3. 2-(imidazol-1-yl)-1-phenylethanone: (m-nitrobenzoic acid) [(L · Hmba), Hmba = m-nitrobenzoic acid] (**3**)*

2-(imidazol-1-yl)-1-phenylethanone (18.6 mg, 0.10 mmol) dissolved in 1 mL ethanol. To this solution, m-nitrobenzoic acid (16.7 g, 0.10 mmol) in 5 mL of ethanol was added. Colorless prisms were obtained after several days of slow evaporation of the solvent, yield: 29 mg, 82.07% (based on L). mp 154–156 °C. Elemental analysis: Calc. for $C_{18}H_{15}N_3O_5$: C, 61.13; H, 4.24; N, 11.88. Found: C, 61.08; H, 4.16; N, 11.83. Infrared spectrum (cm^{-1}): 3666s(ν(OH)), 3375s(ν_{as}(NH)), 3151s(ν_s(NH)), 3078m, 2984s, 2918s, 2496m, 2388m, 2326m, 2082w, 1892m, 1763w, 1714s(ν(C=O)), 1668w, 1642s(ν(C=O)), 1620m, 1536s(ν_{as}(NO$_2$)), 1515m, 1486m, 1448m, 1320s(ν_{as}(NO$_2$)), 1282s(ν(C–O)), 1246m, 1202m, 1162m, 1094m, 1006m, 952w, 877w, 831m, 797w, 724m, 654w, 618w, 525w.

*2.2.4. 2-(imidazol-1-yl)-1-phenylethanone: (5-nitrosalicylic acid) [(HL)$^+$ · (5-nsa$^-$), 5-nsa$^-$ = 5-nitrosalicylate] (**4**)*

2-(imidazol-1-yl)-1-phenylethanone (18.6 mg, 0.10 mmol) dissolved in 1 mL ethanol. To this solution, 5-nitrosalicylic acid (18.3 mg, 0.1 mmol) in 4 mL of ethanol was added. Red prisms were obtained after several days of slow evaporation of the solvent, yield: 29 mg, 78.52% (based on L). mp 186–188 °C. Elemental analysis: Calc. for $C_{18}H_{15}N_3O_6$: C, 58.48; H, 4.06; N, 11.37. Found: C, 58.37; H, 3.96; N, 11.29. Infrared spectrum (cm^{-1}): 3574s (ν(OH)), 3486s(multiple, ν_{as}(NH)), 3338s(ν_s(NH)), 3115m, 3054m, 2972m, 2846m, 2724m, 2432w, 2386m, 2231m, 1996w, 1868w, 1783w, 1692s, 1640s(ν(C=O)), 1612m, 1592s(ν_{as}(COO$^-$)), 1540s(ν_{as}(NO$_2$)), 1521m, 1454w, 1406s(ν_s(COO$^-$)), 1358m, 1314s(ν_s(NO$_2$)), 1240m, 1142m, 1103m, 1074m, 1020m, 946m, 868m, 806m, 757m, 680m, 604m, 558m.

2.3. X-ray crystallography

The X-ray intensity data were measured on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). Data collections and reductions were performed using the SMART and SAINT software [32, 33]. The structures were solved by direct methods, and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using the SHELXTL package [34]. In the absence of significant anomalous scattering, Friedel pairs in **4** have been merged before the final refinement. Hydrogen atom positions for the four structures were generated geometrically. Further details of the structural analysis are summarized in Table 1. Selected bond lengths and angles for compounds **1–4** are listed in Table 2; relevant hydrogen bond parameters are provided in Table 3.

Table 1
Summary of X-ray crystallographic data for compounds **1**–**4**.

	1	**2**	**3**	**4**
Formula	$C_{17}H_{13}N_5O_8$	$C_{36}H_{30}N_6O_{10}$	$C_{18}H_{15}N_3O_5$	$C_{18}H_{15}N_3O_6$
Fw	415.32	706.66	353.33	369.33
T (K)	298(2)	298(2)	298(2)	298(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group	$C2/c$	$P\bar{1}$	$P2_1/c$	$P2_12_12_1$
a (Å)	28.095(3)	7.5314(6)	19.3774(17)	5.3029(5)
b (Å)	5.1869(4)	13.1318(12)	12.0973(11)	15.9360(14)
c (Å)	25.903(2)	17.5069(16)	7.1882(6)	20.2249(19)
α (°)	90	93.1150(1	90	90
β (°)	109.710(1)	102.197(2)	92.062(1)	90
γ (°)	90	100.696(2)	90	90
V (Å^3)	3553.5(5)	1655.1(3)	1683.9(3)	1709.1(3)
Z	8	2	4	4
D_{calcd} (Mg/m^3)	1.553	1.418	1.394	1.435
Absorption coefficient (mm^{-1})	0.126	0.106	0.104	0.110
F(000)	1712	736	736	768
Crystal size (mm^3)	0.48 × 0.22 × 0.11	0.46 × 0.45 × 0.42	0.48 × 0.38 × 0.23	0.50 × 0.38 × 0.36
θ range (°)	2.63–25.02	2.39–25.02	2.69–25.01	2.39–25.02
	$-27 \leqslant h \leqslant 32$	$-8 \leqslant h \leqslant 8$	$-14 \leqslant h \leqslant 22$	$-6 \leqslant h \leqslant 6$
Limiting indices	$-6 \leqslant k \leqslant 6$	$-15 \leqslant k \leqslant 14$	$-14 \leqslant k \leqslant 13$	$-18 \leqslant k \leqslant 18$
	$-30 \leqslant l \leqslant 30$	$-16 \leqslant l \leqslant 20$	$-8 \leqslant l \leqslant 7$	$-20 \leqslant l \leqslant 24$
Reflections collected	8436	8617	8254	8659
Reflections independent (R_{int})	3121 (0.0542)	5734 (0.0316)	2974 (0.0815)	1777 (0.0567)
Goodness-of-fit on F^2	0.848	0.974	1.018	0.958
R indices [$I > 2\sigma I$]	$R_1 = 0.0510$	$R_1 = 0.0490$	$R_1 = 0.0471$	$R_1 = 0.0361$
R indices (all data)	$wR_2 = 0.1339$	$wR_2 = 0.1456$	$wR_2 = 0.1223$	$wR_2 = 0.0915$
Largest diff. peak and hole (e Å^{-3})	0.296, −0.222	0.171, −0.199	0.193, −0.163	0.108, −0.123

Table 2
Selected bond lengths [Å] and angles [°] for **1**–**4**.

1			
N(1)—C(1)	1.315(3)	N(1)—C(3)	1.369(3)
N(1)—C(4)	1.447(3)	O(1)—C(5)	1.213(3)
N(2)—C(1)	1.305(3)	N(2)—C(2)	1.352(4)
O(2)—C(12)	1.236(3)	C(1)—N(1)—C(3)	108.1(2)
C(1)—N(1)—C(4)	125.9(3)	C(3)—N(1)—C(4)	126.0(2)
C(1)—N(2)—C(2)	108.6(3)	N(2)—C(1)—N(1)	109.1(3)
2			
N(1)—C(1)	1.346(3)	N(1)—C(3)	1.377(4)
N(1)—C(4)	1.446(3)	N(2)—C(1)	1.316(4)
N(2)—C(2)	1.376(4)	N(3)—C(12)	1.340(3)
N(3)—C(14)	1.372(4)	N(3)—C(15)	1.450(3)
N(4)—C(12)	1.310(3)	N(4)—C(13)	1.365(4)
O(1)—C(5)	1.207(3)	O(2)—C(16)	1.219(3)
O(3)—C(23)	1.132(3)	O(4)—C(23)	1.216(3)
O(7)—C(30)	1.229(3)	O(8)—C(30)	1.274(3)
C(1)—N(1)—C(3)	106.5(2)	C(1)—N(1)—C(4)	127.6(3)
C(3)—N(1)—C(4)	125.8(3)	C(1)—N(2)—C(2)	105.0(2)
C(12)—N(3)—C(14)	107.6(2)	C(12)—N(3)—C(15)	127.2(3)
C(14)—N(3)—C(15)	125.2(3)	C(12)—N(4)—C(13)	108.5(3)
N(2)—C(1)—N(1)	112.0(3)	N(4)—C(12)—N(3)	109.2(3)
O(4)—C(23)—O(3)	125.0(3)	O(7)—C(30)—O(8)	125.6(3)
3			
N(1)—C(1)	1.332(3)	N(1)—C(3)	1.365(3)
N(1)—C(4)	1.452(3)	N(2)—C(1)	1.314(3)
N(2)—C(2)	1.365(4)	N(3)—C(15)	1.474(4)
O(1)—C(5)	1.210(3)	O(2)—C(12)	1.301(3)
O(3)—C(12)	1.208(3)	C(1)—N(1)—C(3)	107.3(2)
C(1)—N(1)—C(4)	126.2(2)	C(3)—N(1)—C(4)	126.4(2)
C(1)—N(2)—C(2)	105.5(3)	N(2)—C(1)—N(1)	111.4(3)
4			
N(1)—C(1)	1.327(3)	N(1)—C(3)	1.375(4)
N(1)—C(4)	1.457(3)	N(2)—C(1)	1.328(3)
N(2)—C(2)	1.357(4)	N(3)—O(5)	1.225(3)
N(3)—O(6)	1.229(3)	N(3)—C(17)	1.468(4)
O(1)—C(5)	1.218(3)	O(2)—C(12)	1.269(4)
O(3)—C(12)	1.241(3)	O(4)—C(14)	1.345(3)
C(1)—N(1)—C(3)	109.0(2)	C(1)—N(1)—C(4)	125.1(3)
C(3)—N(1)—C(4)	125.9(2)	C(1)—N(2)—C(2)	109.3(3)
N(1)—C(1)—N(2)	107.6(3)	O(3)—C(12)—O(2)	125.0(3)

Table 3
Hydrogen bond distances and angles in studied structures **1**–**4**.

D—H···A	d(D—H) **[**Å]	d(H···A) [Å]	d(D···A) [Å]	<(DHA) [°]
1				
N(2)—H(2)···O(2)#1	0.86	1.84	2.615(3)	148.9
N(2)—H(2)···O(3)#1	0.86	2.34	2.985(4)	132.2
2				
O(3)—H(3)···N(2)#1	0.82	1.80	2.618(3)	172.5
N(4)—H(4)···O(7)#2	0.86	2.65	3.113(3)	115.3
N(4)—H(4)···O(8)#2	0.86	1.76	2.614(3)	170.0
3				
O(2)—H(2)···N(2)	0.82	1.73	2.552(3)	176.4
4				
O(4)—H(4)···O(2)	0.82	1.77	2.504(3)	148.4
N(2)—H(2)···O(3)#1	0.86	1.79	2.652(3)	174.7

Symmetry transformations used to generate equivalent atoms for **1**: #1 $x, y - 1, z$. Symmetry transformations used to generate equivalent atoms for **2**: #1 $x, y + 1, z + 1$; #2 $-x + 1, -y + 1, -z$. Symmetry transformations used to generate equivalent atoms for **4**: #1 $-x + 1, y - 1/2, -z + 1/2$.

3. Results and discussion

3.1. Syntheses and general characterization

2-(imidazol-1-yl)-1-phenylethanone has good solubility in common organic solvents, such as CH_3OH, C_2H_5OH, CH_3CN, $CHCl_3$, and CH_2Cl_2. For the preparation of **1**–**4**, the acidic components were mixed directly with the base in 1:1 ratio in methanol and/or ethanol solvents, which was allowed to evaporate at ambient conditions to give the final crystalline products. The molecular structures and their atom labelling schemes for the four structures are shown in Figs. 1, 3, 5 and 7, respectively.

The elemental analyses for all of the compounds are in good agreement with their compositions. The infrared spectra of **1**–**4** are consistent with their chemical formulas determined by elemental analysis and further confirmed by X-ray diffraction

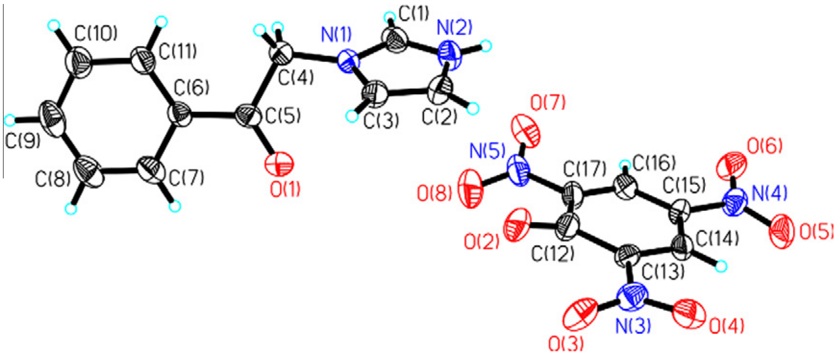


Fig. 1. The structure of **1**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

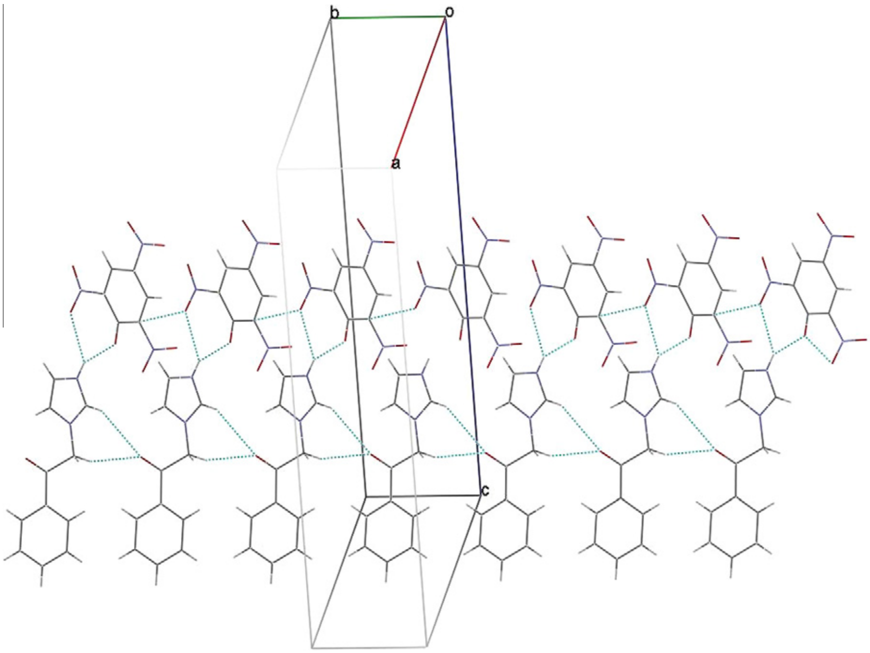


Fig. 2. The 1D chain formed via intrachain O—π, CH—O, and CH_2—O interactions.

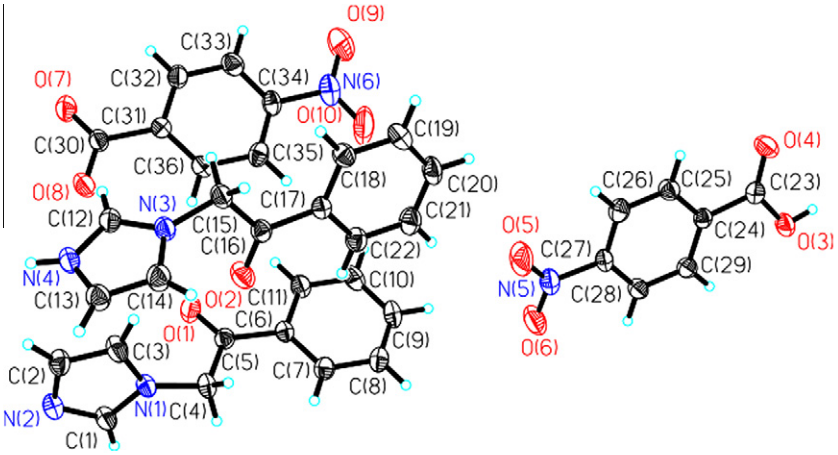


Fig. 3. The structure of **2**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

analysis. The very strong and broad features at 3600–3200 cm^{-1} arise from O—H or N—H stretching frequencies. Benzene and imidazole ring stretching and bending are in the regions of 1500–1630 cm^{-1} and 600–750 cm^{-1}, respectively. The intense peak at ca. 1640 cm^{-1} was derived from the existence of the C=O stretches in the cation.

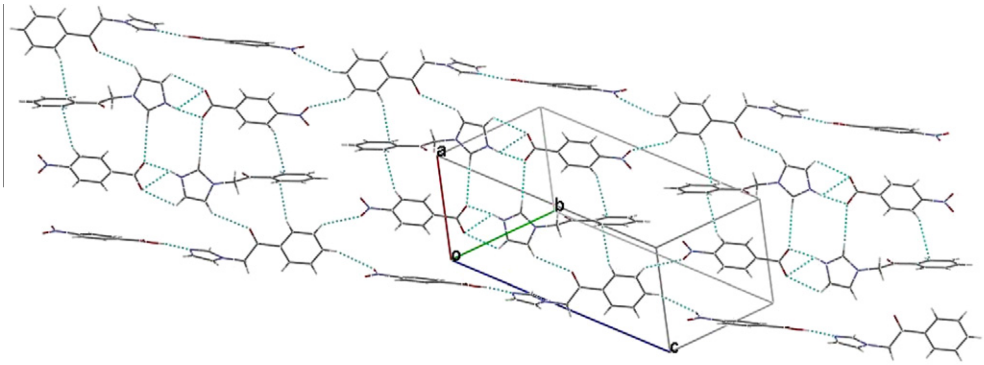


Fig. 4. A double chain structure of **2** when viewed down the *a* axis direction.

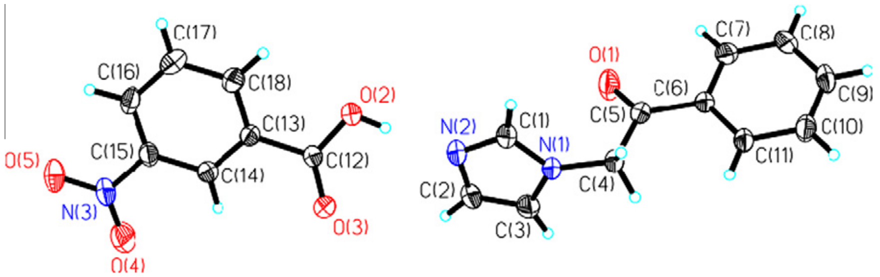


Fig. 5. The structure of **3**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

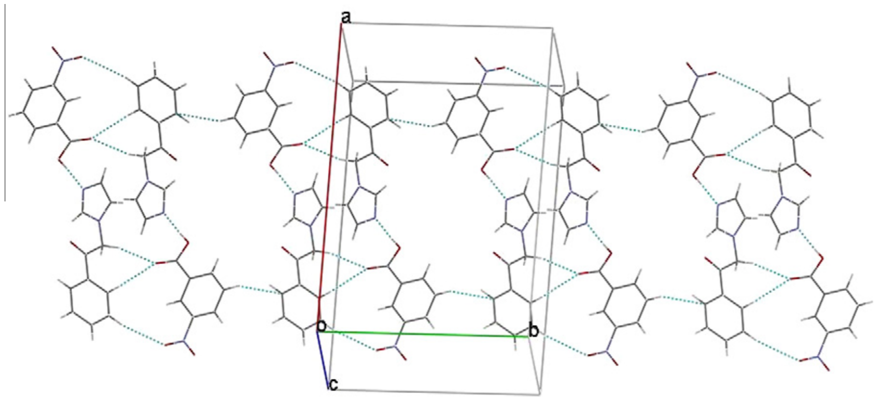


Fig. 6. 1D ladder running along the *b* axis direction.

All of the four adducts except compounds **1**, and **3** show the characteristic bands for COO^-, and compounds **2**, and **3** display strong IR peaks for COOH groups. The intense peak at ca. 1716 cm^{-1} was derived from the existence of the C=O stretches, and the band at ca. 1280 cm^{-1} exhibited the presence of the C—O stretches of the carboxyl group in **2**, and **3**. The presence of two broad bands at ca. 2500 cm^{-1} and 1900 cm^{-1} in compounds **2**, and **3**, characteristic of a neutral O—H···N hydrogen-bond interaction, was viewed as evidence for co-crystal formation [35]. IR spectroscopy has also proven to be useful for the recognition of proton transfer compounds [36]. The most distinct feature in the IR spectrum of proton transfer compounds is the presence of strong asymmetrical and symmetrical carboxylate stretching frequencies at 1550–1610 cm^{-1} and 1300–1420 cm^{-1} in compounds **2**, and **4**, respectively [37].

*3.1.1. X-ray structure of 2-(imidazol-1-yl)-1-phenylethanone: (2,4,6-trinitrophenol) $[(HL)^+ \cdot (pic^-)]$ (**1**)*

Salt **1** was prepared by reacting of a methanol solution of 2,4,6-trinitrophenol and 2-(imidazol-1-yl)-1-phenylethanone in 1:1 ratio. The asymmetric unit of **1** consists of one cation of 2-(imidazolium-1-yl)-1-phenylethanone and one anion of picrate (Fig. 1). This is a salt where the OH groups of 2,4,6-trinitrophenol are ionized by proton transfer to the nitrogen atom (N(2)) of the 2-(imidazol-1-yl)-1-phenylethanone moieties, which is also confirmed by the bond distance of O(2)—C(12) (1.236(3) Å) for phenolate (1.24 ± 0.01 Å) [38]. In the compound, there is one pair of ion pair with no included solvent molecules. First of all, an examination of the data in Table 2 shows that the distance value of C5—O1 (1.213 Å) in the cation clearly exhibits double-bond character. Thus there is no keto-enol tautomerism which is due to the absence of strong intramolecular and intermolecular hydrogen bonding that can produce a hydrogen bonded stable ring such as 5-, and 6-membered rings. This is also reflected by the bond of C4—C5 (1.509(4)) Å, which is a typical single bond. The O atom of the carbonyl group in the cation is at the trans position in respect to the H at the N—CH—N of the cation.

In the solid state, there is consistently ionic hydrogen bond formed between the imidazolium NH^+ cation, and the 2,4,6-trinitrophenolate anion.

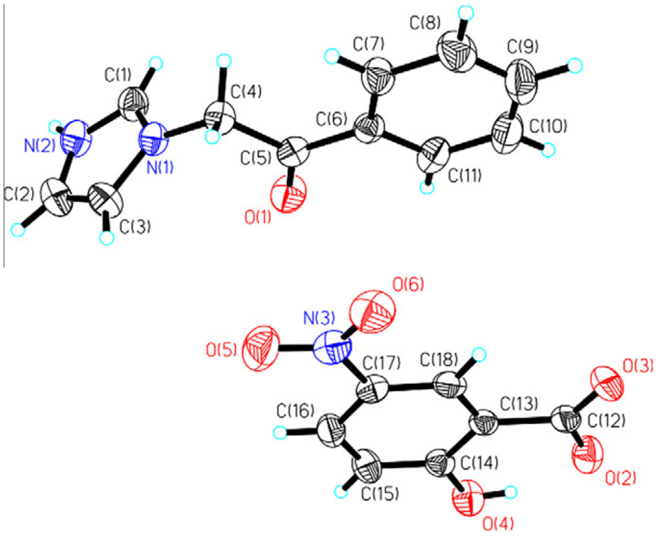


Fig. 7. The structure of **4**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

The ortho-nitro groups (N3—O3—O4, and N5—O7—O8) deviate from the benzene plane and have dihedral angles of 9.3°, and 21.6° with the benzene plane, which are smaller than the corresponding values of the reported salts based on picrates [39]. The para-nitro group [N4—O5—O6] also deviates by 10.4° from the benzene plane, which is larger than the corresponding data reported by Muthamizhchelvan et al. [39]. The interplane angle between the benzene ring of the picrate and the imidazole ring is 8.5° indicating the coplanarity of both rings.

One anion is bound to one cation to generate a heteroadduct through two N-H···O hydrogen bonds with N—O distance of 2.615(3)–2.985(4) Å. Of the two N—H···O hydrogen bonds one is between the NH^+ and the phenolate group, the other is between the NH^+ group and the para-NO_2 group. Under the bifurcated hydrogen bonding interactions the anion and the cation made a $R_1^2(6)$ ring motif according to Bernstein [40].

Such heteroadducts were held together via the O—π (between the O atom of the nitro group and the benzene ring of the anion with O—Cg distance of 3.16 Å), CH—O (between N—CH—N of the cation and the carbonyl group of its neighboring cation with C—O distance of 3.42 Å), and CH_2—O interactions (between CH_2 of the cation and the C=O of its neighboring cation with C—O distance of 3.31 Å). In this case the O—Cg distance is comparable to the archived data (3.12 Å) [41]. For the presence of such kind of interactions two cations generated a $R_2^1(6)$ graph set.

Through these interactions the heteroadducts were connected together to form a 1D chain (A) running along the *b* axis direction (Fig. 2). There are also 1D chain (B) running along the *b* axis direction composed of the above heteroadducts, yet the cations on the (B) chain were antiparallel to the cations at the (A) chain, and the anions on the (B) chain formed an angle of ca. 82° with the anions on the (A) chain. The A chains and the B chains were joined together by the interchain CH—O interactions between the benzene CH of the cation and the para-nitro group with C—O distance of 3.54 Å, and CH—C(carbonyl) interaction between the benzene CH of the cation and the C=O group of the neighboring chain with C—C distance of 3.55 Å to form a double chain extending along the *b* axis direction. The double chains were further linked together via the CH—O interaction between the benzene CH of the anion and the o-nitro group with C—O distance of 3.20 Å along the *c* axis direction to form a 2D sheet extending on the *bc* plane. The sheets were further stacked along the *a* axis direction by the intersheet CH—O, and CH_2—O interactions to form a 3D network structure. In this case the anions and the cations at the adjacent sheets were slipped some distance from each other along the *c* axis direction. It is worthy to point out that the third sheet has the same project on the *bc* plane as the first sheet, so does the second sheet and the fourth sheet.

*3.1.2. X-ray structure of 2-(imidazol-1-yl)-1-phenylethanone: (p-nitrobenzoic acid)[$(HL)^+ \cdot L \cdot Hnbd \cdot (nbd)^-$] (**2**)*

There are one protonated L, one molecule of L, one molecule of p-nitrobenzoic acid, and one anion of p-nitrobenzoic acid in the asymmetric unit of salt **2** (Fig. 3).

Similar to **1**, the bond distances of C5—O1(1.207(3) Å) and C16—O2 (1.219(3) Å) in the neutral L and in the cation clearly exhibit typical double-bond characters. The C—O distances of the COOH in the p-nitrobenzoic acid are ranging from 1.216(3) [O(4)—C(23)] to 1.312(3) Å [O(3)—C(23)] with the Δ value of 0.096 Å, which suggests that the carboxyl group is protonated. While the C—O bond distances in the carboxylate group are 1.229(3) and 1.274(3) Å (Δ is 0.045 Å) with the mean value of 1.251 Å which is shorter than the C—O single bond (1.312(3) Å) and larger than the C=O double bond (1.216(3) Å). The O atoms of the carbonyl groups in the cation and the neutral L are both at the trans positions in respect to the corresponding Hs at the N—CH—N groups.

One L and one Hnbd form a heteroadduct (A) through the neutral hydrogen bond (O(3)—H(3)···N(2)#1, 2.618(3) Å). One HL^+ cation and one nbd^- anion also formed a heteroadduct (B) through two N—H···O hydrogen bonds with N-O distances of 2.614(3) and 3.113(3) Å, and one CH—O association between 4-CH of the imidazole cation and the carboxylate with C—O distance of 3.08 Å. For the presence of such interactions the anion and the cation generated close joint $R_1^2(4)$, and $R_2^1(5)$ motifs. The heteroadduct (A) and heteroadduct (B) were connected together via CH—π and CH—O interactions to form a tetra-component adduct. The adjacent tetra-component adducts were combined together by the CH—O interaction between the benzene CH of the cation and the nitro group with C—O distance of 3.31 Å, and 3.57 Å respectively to form a 1D chain running along the *b* axis direction. Two such parallel chains were joined together via the CH—O interaction between the N—CH—N and the carboxylate with C—O distance of 3.42 Å, and CH—π interaction between the benzene CH of the anion and the benzene ring of the cation with C—Cg distance of 3.67 Å to form a double chain (Fig. 4). The double chains were arranged parallelly on the *bc* plane, but there are no connections between them. The double chains were stacked along the *a* axis direction via the CH—O, CH—π, and CH_2—O interactions to form a 3D network structure. Here the adjacent double chains were slipped some distance from each other along the *c* axis direction such that one double chain of the first layer is connected with two double chains of the second layer.

*3.1.3. X-ray structure of 2-(imidazol-1-yl)-1-phenylethanone: (m-nitrobenzoic acid) ($L \cdot Hmbd$) (**3**)*

Similar to **2**, the compound **3** of the composition ($L \cdot Hmbd$) was prepared by reacting equal mol of L and m-nitrobenzoic acid, in which no proton of the m-nitrobenzoic acid was transferred to the ring N atom of the L. Thus **3** can be classified as an organic co-crystal. In the asymmetric unit of **3** there existed one molecule of L, and one molecule of m-nitrobenzoic acid, as shown in Fig. 5.

The bond C5—O1 (1.210(3) Å) in the L is also a typical C=O. The C—O distances of the COOH group of the m-nitrobenzoic acid are ranging from 1.208(3) to 1.301(3) Å. The difference (Δ is 0.093 Å) in bond distances between O(2)—C(12) (1.301(3) Å) and O(3)—C(12) (1.208(3) Å) in the carboxyl group is expected for unionized COOH group. Different from **1**, and **2**, the O atom of the carbonyl group in the L is at the syn position in respect to the H at the N—CH—N group.

One Hmbd and one L form a heteroadduct by the neutral hydrogen bond (O(2)—H(2)$\cdots$N(2), 2.552(3) Å) between the OH group of the m-nitrobenzoic acid and the ring N atom of L. Two adjacent heteroadducts were joined together by the CH—O, and CH_2—O interactions to form a tetra-component adduct. There are two kinds of CH—O interactions in the tetra-component adduct: one kind is between the benzene CH of L and the carbonyl group of the Hmbd with C—O distance of 3.54 Å, the other kind is between the benzene CH of L and the NO_2 group of the m-nitrobenzoic acid with C—O distance of 3.61 Å. The CH_2—O interaction exists between the CH_2 moiety of the L and the C=O of the m-nitrobenzoic acid with C—O distance of 3.19 Å. In the tetra-component adduct the two m-nitrobenzoic acids and the two L were antiparallelly arranged. Under these noncovalent interactions there are close joint $R_2^1(7)$ and $R_2^2(11)$ ring motifs. The tetra-component adducts were connected together via the CH—π interaction between 5-CH of m-nitrobenzoic acid and L with C—Cg distance of 3.77 Å to form a ladder running along the *b* axis direction (Fig. 6). The ladders were stacked along the *c* axis direction via the CH—O, π—π (between the benzene ring of the acid and the benzene ring of L at the adjacent ladders with Cg—Cg distance of 3.30 Å), and CH_2—O interactions (between CH_2 of L and the carbonyl group of the Hmbd at the neighboring ladder with C—O distance of 3.28 Å) to form a 3D network structure. It should be noted that the adjacent ladders were not parallel to each other, they made an angle of ca. 30° with each other. In the 3D structure the third ladder has the same project on the *ab* plane as the first ladder, so does the second ladder and the fourth ladder. For the presence of such a stacking mode, in the whole structure of **3** there are no channels.

3.1.4. X-ray structure of 2-(imidazol-1-yl)-1-phenylethanone: (5-nitrosalicylic acid)[$(HL)^+ \cdot (5\text{-nsa}^-)$] (4)

The asymmetric unit of **4** consists of one cation of L, and one anion of 5-nitrosalicylate (Fig. 7). This is a salt where the COOH groups of 5-nitrosalicylic acids are ionized by proton transfer to the nitrogen atoms of the 2-(imidazol-1-yl)-1-phenylethanone moieties, which is also confirmed by the bond distances of O(3)—C(12) (1.241(3) Å) and O(2)-C(12) (1.269(4) Å) for the carboxylate.

The same as **1**, and **2**, O atom of the C=O in the cation is at the trans position in respect to the H at the N—CH—N unit. The rms deviations of the imidazole and the benzene rings in the cation are 0.0038, and 0.0040 Å, respectively. The two rings are almost perpendicular to each other with dihedral angle of 83.4°.

Because of the presence of the intramolecular hydrogen bond between the carboxylate group and the phenol group (O(4)—H(4)$\cdots$O(2), 2.504(3) Å), it is generally expected and found that the carboxylate group is essentially coplanar with the benzene ring [torsion angle C14—C13—C12—O3, 177.13°]. This feature is similar to that found in the salicylic acid [42], and in the previously reported structure of proton-transfer compound based on 5-nsa^- [43]. As expected the O—O separation is essentially in the range of the documented data [2.489–2.509 Å] [43] because of the planarity of the hydrogen bonded carboxylate unit, but it is slightly contracted compared with the nonproton transfer examples (2.547–2.604 Å, mean: 2.588 Å), as a result of deprotonation. The 5-nitro group also varies little conformationally [torsion angle C16—C17—N3—O6, 175.33°] compared with the reported data within this set of compounds (175.4–180°) [43].

One anion was bonded to one cation through the hydrogen bond (N(2)—H(2)$\cdots$O(3)#1, 2.652(3) Å) between the NH^+ cation and the carboxylate to form a heteroadduct. So in the solid state, there is consistently ionic hydrogen bond produced between the NH^+ cation, and the 5-nitrosalicylate ion, which is to be expected [44].

The adjacent heteroadducts were held together by the CH—O interaction between the nitro group and the benzene CH of the cation with C—O distance of 3.52 Å to form a 1D chain running along the *b* axis direction. Such chains were further joined together via the interchain CH—O interactions to form a 2D sheet extending on the *ab* plane (Fig. 8). Of these interchain CH—O interactions one kind of CH—O interaction is found between the nitro group and 4-CH of the imidazole with C—O distance of 3.31 Å, the other kind of CH—O interaction is formed between 5-CH of the imidazole and the C=O group of the neighboring cation with C—O distance of 3.17 Å. The sheets were further stacked along the *c* axis direction by the CH—O (between the benzene CH of the cation and the C=O group of the cation belonging to adjacent sheets with C—O distance of 3.39 Å), and CH—π interactions (between the benzene CH of the cation and the imidazole ring with C—Cg distance of 3.72 Å) to form a 3D network structure. In this case the adjacent

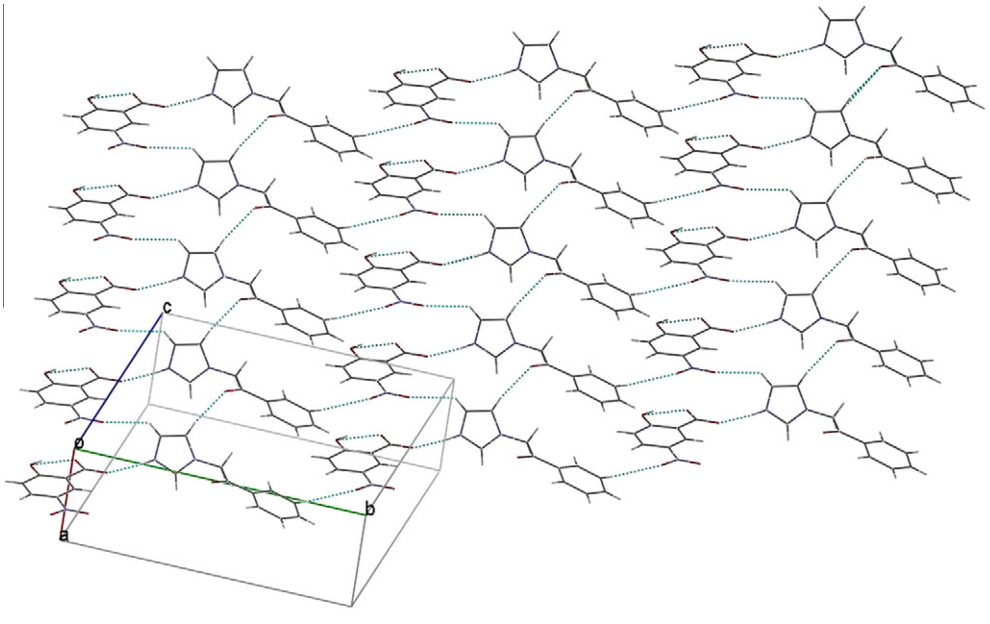


Fig. 8. 2D sheet structure of **4** extending along the *ab* plane.

sheets were slipped some distance from each other that the cations of adjacent sheets were not parallel to each other, while the anions belonging to adjacent sheets were antiparallelly arranged.

4. Conclusion

Four organic acid–base adducts with 3D network structure have been prepared and structurally characterized. Despite variations in molecular shape on the acidic components, there all exist strong intermolecular hydrogen bonds between the acidic components and the 2-(imidazol-1-yl)-1-phenylethanone.

In the compounds **1**, **2**, and **4**, the imidazolium cations function as acceptors for ionic hydrogen bonds that organize and orient the anions, while in compound **3** the imidazole fragments function as acceptors for neutral hydrogen bonds. This study has demonstrated that the N—H···O hydrogen bond is the primary intermolecular force in a family of structures containing the OH···im synthons. In addition two types of secondary C-H···O hydrogen bond (intra- and interchain C—H···O contacts) were observed, and both have the same metrics in structure extension. There are also CH_2—O, CH—π, π—π, and O—π interactions in these compounds.

The results presented herein indicate that the strength and directionality of the N^+—H···O^-, O—H···O, and O—H···N hydrogen bonds (ionic or neutral) between acidic components and 2-(imidazol-1-yl)-1-phenylethanone are sufficient to bring about the formation of binary organic salts or cocrystals.

Supporting Information Available

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic data center, CCDC Nos. 800022 for **1**, 800078 for **2**, 800872 for **3**, and 799295 for **4**. Copies of this information may be obtained free of charge from the +44 1223 336 033 or Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

Acknowledgment

We gratefully acknowledge the financial support of the Education Office Foundation of Zhejiang Province (project No. Y201017321) and the financial support of the Zhejiang A & F University Science Foundation (Project No. 2009FK63).

References

[1] (a) C.J. Janiak, J. Chem. Soc., Dalton Trans. (2000) 3885;
(b) G.R. Desiraju, Chem. Commun. (2005) 2995.
[2] (a)J.M. Lehn, J.L. Atwood, J.E.D. Davies, D.D. MacNicol, F. Vögtle (Eds.), Comprehensive Supramolecular Chemistry, Pergamon, Oxford, UK, 1996;
(b) P.A. Wood, F.H. Allen, E. Pidcock, CrystEngComm. 11 (2009) 1563;
(c) D.Ž. Veljković, G.V. Janjić, S.D. Zarić, CrystEngComm. 13 (2011) 5005;
(d) G.R. Desiraju, Cryst. Growth Des. 11 (2011) 896.
[3] N. Shan, A.D. Bond, W. Jones, Cryst. Eng. 5 (2002) 9.
[4] D.R. Weyna, T. Shattock, P. Vishweshwar, M.J. Zaworotko, Cryst. Growth Des. 9 (2009) 1106.
[5] M. Du, Z.H. Zhang, X.J. Zhao, Cryst. Growth Des. 5 (2005) 1247.
[6] B.R. Bhogala, A. Nangia, Cryst. Growth Des. 3 (2003) 547.
[7] E. Weber, Design of Organic Solids. Topics in Current Chemistry, Springer, Berlin, 1998. 198.
[8] B.R. Bhogala, Cryst. Growth. Des. 3 (2003) 547.
[9] M. Du, Z.H. Zhang, X.J. Zhao, Cryst. Growth. Des. 5 (2005) 1199.
[10] T.R. Shattock, P. Vishweshwar, Z.Q. Wang, M.J. Zaworotko, Cryst. Growth. Des. 5 (2005) 2046.
[11] M. Sarkar, K. Biradha, Cryst. Growth. Des. 6 (2006) 202.
[12] A. Ballabh, D.R. Trivedi, P. Dastidar, Cryst. Growth. Des. 5 (2005) 1545.
[13] D.R. Trivedi, P. Dastidar, Cryst. Growth. Des. 6 (2006) 1022.
[14] C.B. Aakeröy, A.M. Beatty, B.A. Helfrich, Angew. Chem. Int. Ed. 40 (2001) 3240.
[15] J.C. MacDonald, P.C. Dorrestein, M.M. Pilley, Cryst. Growth. Des. 1 (2001) 29.
[16] D.R. Trivedi, A. Ballabh, P. Dastidar, CrystEngComm. 5 (2003) 358.
[17] Y. Akhriff, J. ServerCarrio, J. Garcia-Lozano, J.V. Folgado, A. Sancho, E. Escriva, P. Vitoria, L. Soto, Cryst. Growth. Des. 6 (2006) 1124.
[18] C.B. Aakeröy, D.J. Salmon, B. Leonard, J.F. Urbina, Cryst. Growth. Des. 5 (2005) 865.
[19] C.B. Aakeröy, D.J. Salmon, M.M. Smith, J. Desper, Cryst. Growth. Des. 6 (2006) 1033.
[20] L.E. Cheruzel, M.S. Mashuta, R.M. Buchanan, Chem. Commun. 2223 (2005).
[21] P.V. Roey, K.A. Bullion, Y. Osawa, R.M. Bowman, D.G. Braun, Acta Crystallogr. C47 (1991) 1015.
[22] B.Q. Ma, P. Coppens, Cryst. Growth. Des. 4 (2004) 1377.
[23] B.M. Ji, F.F. Jian, P.P. Sun, C.X. Du, K.L. Ding, Z. Kristallogr. NCS 219 (2004) 466.
[24] B.M. Ji, C.X. Du, Y. Zhu, K.L. Ding, J. Chem. Crystallogr. 30 (2000) 783.
[25] B.M. Ji, D.S. Deng, N. Ma, S.B. Miao, X.G. Yang, L.G. Ji, M. Du, Cryst. Growth. Des. 10 (2010) 3060.
[26] B.M. Ji, F.F. Jian, H.L. Xiao, C.X. Du, Anal. Sci.: X-ray Struct. Anal. 20 (2004) x101.
[27] X.M. Song, J.J. Li, X.H. Liu, C.X. Ren, S.M. Shang, Acta Cryst. E67 (2011) o179.
[28] S.W. Jin, W.B. Zhang, D.Q. Wang, H.F. Gao, J.Z. Zhou, R.P. Chen, X.L. Xu, J. Chem. Crystallogr. 40 (2010) 87.
[29] S.W. Jin, D.Q. Wang, Z.J. Jin, L.Q. Wang, Polish J. Chem. 83 (2009) 1937.
[30] S.W. Jin, D.Q. Wang, J. Chem. Crystallogr. 40 (2010) 914.
[31] I.C. Lennon, J.A. Ramsden, Org. Process Res. Dev. 9 (2005) 110.
[32] R.H. Blessing, Acta Crystallogr. A51 (1995) 33.
[33] G.M. Sheldrick, SADABS "Siemens Area Detector Absorption Correction", University of Göttingen, Göttingen, Germany, 1996.
[34] G.M. Sheldrick, Acta Cryst. A64 (2008) 112.
[35] C.B. Aakeröy, J. Desper, M.E. Fasulo, CrystEngComm. 8 (2006) 586.
[36] (a) D.E. Lynch, L.C. Thomas, G. Smith, K.A. Byriel, C.H.L. Kennard, Aust. J. Chem. 51 (1998) 867;
(b) G. Smith, J.M. White, Aust. J. Chem. 54 (2001) 97.
[37] D.H. Williams, I. Fleming, Spectroscopic Methods in Organic Chemistry, fifth ed., McGraw-hill, London, 1995.
[38] (a) T. Kagawa, R. Kawai, S. Kashino, M. Haisa, Acta Crystallogr. B32 (1976) 3171;
(b) K. Maartmann-Moe, Acta Crystallogr. B25 (1969) 1452;
(c) G.J. Palenik, Acta Crystallogr. B28 (1972) 1633;
(d) A.N. Talukdar, B. Chaudhuri, Acta Crystallogr. B32 (1976) 803;
(e) G. Ferguson, B. Kaitner, D. Lloyd, H. McNab, J. Chem. Res. (S) (1984) 182;
(f) W. Sawka-Dobrowolska, E. Grech, B. Brzezinski, Z. Malarski, L. Sobczyk, J. Mol. Struct. 356 (1995) 117;
(g) I. Majerz, Z. Malarski, L. Sobczyk, Chem. Phys. Lett. 274 (1997) 361.
[39] C. Muthamizhchelvan, K. Saminathan, J. Fraanje, R. Peschar, K. Sivakamar, Anal. Sci. 21 (2005) X61.
[40] J. Bernstein, R.E. Davis, L. Shimoni, N.L. Chang, Angew. Chem. Int. Ed. 34 (1995) 1555.
[41] C. Biswas, M.G.B. Drew, D. Escudero, A. Frontera, A. Ghosh, Eur. J. Inorg. Chem. (2009) 2238.
[42] M. Sundaralingam, L.H. Jensen, Acta Crystallogr. 18 (1965) 1053.
[43] G. Simith, A.W. Hartono, U.D. Wermuth, P.C. Healy, J.M. White, A.D. Rae, Aust. J. Chem. 58 (2005) 47.
[44] M. Felloni, A.J. Blake, P. Hubberstey, C. Wilson, M. Schröder, CrystEngComm. 4 (2002) 483.