

UDC 548.737

SUPRAMOLECULAR ARCHITECTURE OF A 1:1 COMPLEX
OF 5-AMINOISOPHTHALIC ACID WITH 1,2-BIS(4-PYRIDYL)ETHANES.F. Lush¹, F.M. Shen²¹Department of General Education Center, Yuanpei University, HsinChu, Taiwan

E-mail: lush@mail.ypu.edu.tw

²Department of Biotechnology, Yuanpei University, HsinChu, Taiwan

E-mail: fmshen@mail.ypu.edu.tw

Received March, 3, 2013

Revised — July, 23, 2013

The crystal structure has been solved for a 1:1 molecular complex of 5-aminoisophthalic acid and 1,2-bis(4-pyridyl)ethane. Crystal data: $C_{20}H_{19}N_3O_4$, $M = 365.38$, orthorhombic, $P2_1/n$ space group; unit cell parameters: $a = 10.7521(6) \text{ \AA}$, $b = 11.9151(6) \text{ \AA}$, $c = 13.7645(8) \text{ \AA}$, $V = 1763.40(17) \text{ \AA}^3$, $Z = 4$, $d_x = 1.376 \text{ g/cm}^3$, $R_1 = 0.0514$, $T = 110 \text{ K}$. The 5-aminoisophthalic acid molecule is linked by O—H \cdots N hydrogen bond to 1,2-bis(4-pyridyl)ethane, forming a linear hydrogen bonded chain running parallel to [0 3 0]. In the crystal, the intermolecular interactions link 5-aminoisophthalic acid molecules with head-to-head N—H \cdots O hydrogen bonds generating $R_2^2(14)$ centrosymmetric dimers, which are extended head-to-tail via amine and carboxyl group N—H \cdots O=C hydrogen bond. The supramolecular structure is consolidated by C—H \cdots O hydrogen bonds and $\pi\cdots\pi$ interactions.

Keywords: 5-aminoisophthalic acid, 1,2-bis(4-pyridyl)ethane, hydrogen bonding, centrosymmetric, supramolecular.

The 1,2-bis(4-pyridyl)ethane is a versatile spacer and a useful component in the construction of supramolecular architectures both by means of protonation at pyridine nitrogen involving $N^+—H\cdots O^-$ synthon and through formation of co-crystal involving N \cdots H—O hydrogen bonds [1, 2]. Each of the pyridyl nitrogen atoms acts as a hydrogen bond acceptor, forming linear hydrogen-bonded associations [3–5]. The structures of a number of 1:1 adducts of benzoic acid derivatives with 1,2-bis(4-pyridyl)ethane have been reported [6, 8]. Not only benzoic acid derivatives are more effective for the promotion of hydrogen-bonding extensions, but also from various weak noncovalent interactions, such as π - π stacking and C—H \cdots π interactions.

This study is the continuation of our research [9, 10] on the complexes formed by 1,2-bis(4-pyridyl)ethane (**Bpe**) with 5-aminoisophthalic acid (**Apa**). We present here the crystal structure of the 5-aminoisophthalic acid and 1,2-bis(4-pyridyl)ethane 1:1 adduct. The structure of the title compound comprises 1,2-bis(4-pyridyl)ethane molecule and 5-aminoisophthalic acid molecule, with no proton transfer. Neutral molecules connected via O—H \cdots N hydrogen-bonds leading to chains is found in the 1:1 co-crystals.

EXPERIMENTAL

Materials and methods. All chemicals purchased were reagent grade and used without further purification. Elemental analysis (C, H and N) was performed on a Heraeus CHN—O-Rapid elemental analyzer. FT-IR spectra were recorded in the range 400—4000 cm^{-1} on a JASCO 6200 FT-IR spectrophotometer using a KBr pellet.

Table 1

Crystal data, experimental details and refinement parameters for the structure of [C₁₂H₁₂N₂·C₈H₇NO₄]

| | |
|--|--|
| Chemical formula | [C ₁₂ H ₁₂ N ₂ ·C ₈ H ₇ NO ₄] |
| Molecular weight | 365.38 |
| Temperature, K | 110(2) |
| Wavelength, Å | 0.71073 |
| Crystal system | Orthorhombic |
| Space group | <i>P</i> 2 ₁ / <i>n</i> |
| Unit cell parameters, <i>a</i> , <i>b</i> , <i>c</i> , Å | 10.7521(6), 11.9151(6), 13.7645(8) |
| Volume, Å ³ | 1763.40(17) |
| <i>Z</i> | 4 |
| <i>d_x</i> , g/cm ³ | 1.376 |
| Extinction coefficient, mm ⁻¹ | 0.098 |
| <i>F</i> (000) | 768 |
| Crystal size, mm | 0.28×0.26×0.08 |
| <i>h</i> , <i>k</i> , <i>l</i> limits | -12 ≤ <i>h</i> ≤ 12, -13 ≤ <i>k</i> ≤ 14, -16 ≤ <i>l</i> ≤ 12 |
| Data completeness on θ , deg. | 2.95—25.20, 99.8 % |
| Measured / independent reflections | 7358 / 3169 [<i>R</i> (int) = 0.0499] |
| Reflections with <i>I</i> > 2 σ (<i>I</i>) | 2387 |
| Number of parameters | 3399 |
| Transmission | 0.98517—1.00000 |
| Refinement | Full-matrix least squares against <i>F</i> ² |
| GOOF against <i>F</i> ² | 0.942 |
| Final <i>R</i> factor <i>I</i> > 2 σ (<i>I</i>) | <i>R</i> ₁ = 0.0514, <i>wR</i> ₂ = 0.1314 |
| <i>R</i> factor (all data) | <i>R</i> ₁ = 0.0690, <i>wR</i> ₂ = 0.1372 |
| Residual electron density, e/Å ⁻³ | -0.473 and 0.061 |
| CCDC deposition number | 917169 |

X-ray crystallographic analysis. Diffraction data of the title compound were collected at 110 K on a Oxford Diffraction Gemini-S CCD diffractometer with graphite-monochromatized MoK α radiation ($\lambda = 0.71073$ Å) in multi-scan mode. The structure was solved by direct methods using the program SHELXS-97 [11] and refined by full-matrix least-squares methods on *F*² using the program SHELXL-97. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions, with O—H = 0.84, C—H = 0.95 (aromatic), and 0.99 Å (methyl), and refined in the riding model with *U*_{iso}(H) = 1.5_{eq}(C) for methyl and *U*_{iso}(H) = 1.2_{eq}(C) for others. Besides, H atoms can also localize in the hydrogen bonds, but we found the two methods to localize hydrogen atoms are in the same position. The crystallographic data and experimental details for structural analyses are summarized in Table 1.

Structural CIF file containing complete information on the studied structure was deposited with CCDC, deposition number 917169, and is freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/cif.

Synthesis. The 5-aminoisophthalic acid (0.0362 g, 0.20 mmol) and 1,2-bis(4-pyridyl)ethane (0.0369 g, 0.20 mmol) were dissolved in 20 mL methanol-water (1:1), the solution was refluxed for 30 min. The filtered solution was transferred to a 25 mL tube. After one week at room temperature colorless transparent crystals were obtained (yield 55 %). We have also attempted mixing the components in the solution at room temperature no crystallization occurred even in three weeks. Elemental analysis calcd. for C₂₀H₁₉N₃O₄ (*M*_r = 365.38): C 65.69, H 5.24, N 11.49 %. Found: C 66.03, H 5.29,

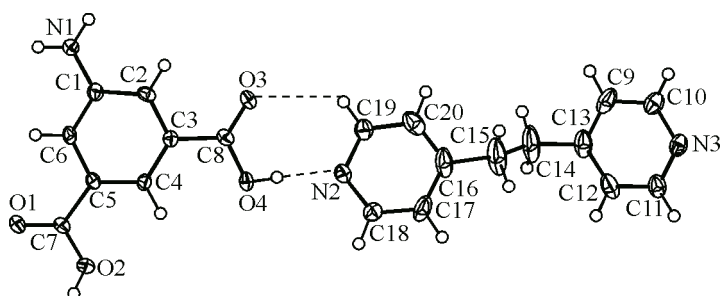


Fig. 1. View of the 1:1 molecular associate in the structure of the title compound with atomic labeling. Thermal ellipsoids are drawn at the 50 % probability level

N 11.75 %. IR (KBr, ν , cm^{-1}): 3446(s), 3366(s), 1701(s), 1645(w), 1608(s), 1459(m), 1421(s), 1415(s), 1359(m), 1279(s), 1204(m), 899(m), 818(m), 769(w).

RESULTS AND DISCUSSION

The ORTEP view of the title compound is shown in Fig. 1. The bond lengths and angles are listed in Table 2 and 3. The asymmetric unit is composed of one molecule of Bpe and one molecule of Apa, with no proton transfer. In the structure, the molecules associate 5-aminoisophthalic acid and 1,2-bis(4-pyridyl)ethane via carboxylic and pyridine group O—H \cdots N, forming linear hydrogen bonding

Table 2

Bond lengths d , Å in the structure of $[\text{C}_{12}\text{H}_{12}\text{N}_2 \cdot \text{C}_8\text{H}_7\text{NO}_4]$

| Bond | d | Bond | d | Bond | d | Bond | d |
|-------|----------|--------|----------|---------|----------|---------|----------|
| O1—C7 | 1.213(3) | C3—C4 | 1.389(4) | N2—C19 | 1.340(4) | C13—C14 | 1.503(5) |
| O3—C8 | 1.213(3) | C3—C8 | 1.494(3) | C5—C4 | 1.395(3) | C16—C20 | 1.367(6) |
| O4—C8 | 1.319(3) | N3—C10 | 1.338(4) | C5—C7 | 1.492(4) | C16—C17 | 1.391(5) |
| C2—C1 | 1.393(3) | N3—C11 | 1.337(3) | C18—C17 | 1.359(5) | C16—C15 | 1.510(5) |
| C2—C3 | 1.387(4) | O2—C7 | 1.319(3) | C10—C9 | 1.378(5) | C12—C11 | 1.382(4) |
| C6—C5 | 1.387(4) | N1—C1 | 1.389(4) | C13—C12 | 1.373(6) | C19—C20 | 1.362(4) |
| C6—C1 | 1.389(4) | N2—C18 | 1.327(4) | C13—C9 | 1.398(5) | C15—C14 | 1.408(6) |

Table 3

Bond angles ω , deg. in the structure of $[\text{C}_{12}\text{H}_{12}\text{N}_2 \cdot \text{C}_8\text{H}_7\text{NO}_4]$

| Angles | ω | Angles | ω | Angles | ω |
|------------|------------|-------------|------------|-------------|------------|
| C1—C2—C3 | 120.43(24) | C4—C5—C7 | 122.92(21) | C9—C13—C14 | 122.42(32) |
| C5—C6—C1 | 121.31(24) | N2—C18—C17 | 123.18(30) | C20—C16—C17 | 116.80(37) |
| C4—C3—C2 | 120.97(25) | N3—C10—C9 | 122.43(29) | C20—C16—C15 | 119.91(36) |
| C4—C3—C8 | 122.22(22) | O3—C8—O4 | 123.07(25) | C17—C16—C15 | 122.96(32) |
| C2—C3—C8 | 116.78(23) | O3—C8—C3 | 122.54(22) | C10—C9—C13 | 120.42(33) |
| C10—N3—C11 | 117.66(25) | O4—C8—C3 | 114.39(23) | C18—C17—C16 | 119.83(33) |
| N1—C1—C2 | 121.11(24) | C3—C4—C5 | 118.74(22) | C13—C12—C11 | 120.82(34) |
| N1—C1—C6 | 120.39(24) | O1—C7—O2 | 123.04(25) | N2—C19—C20 | 123.10(26) |
| C2—C1—C6 | 118.48(22) | O1—C7—C5 | 122.16(22) | N3—C11—C12 | 122.50(25) |
| C18—N2—C19 | 116.91(26) | O2—C7—C5 | 114.80(23) | C19—C20—C16 | 120.08(34) |
| C6—C5—C4 | 120.06(24) | C12—C13—C9 | 116.16(37) | C14—C15—C16 | 119.03(32) |
| C6—C5—C7 | 116.99(23) | C12—C13—C14 | 121.32(36) | C15—C14—C13 | 112.31(32) |

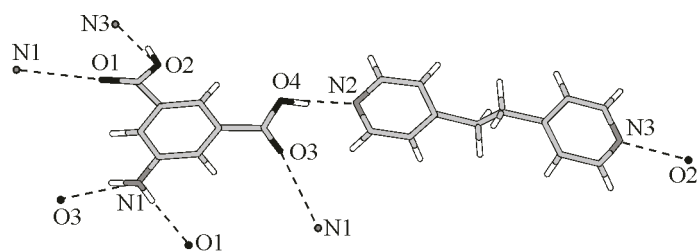


Fig. 2. Fragment of the structure that illustrates the hydrogen bonds

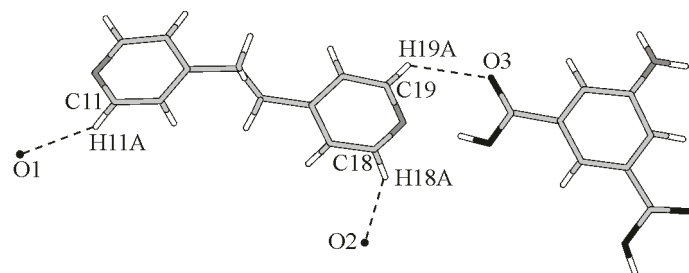


Fig. 3. Fragment of the structure that illustrates non-classical hydrogen bonds

Table 4

Parameters of the hydrogen bonds (Å, deg.)

| D—H...A | <i>d</i> (D—H) | <i>d</i> (H...A) | <i>d</i> (D...A) | ∠DHA | Symmetry operations |
|---------------|----------------|------------------|------------------|------|------------------------|
| N1—H1A...O1 | 0.90 | 2.15 | 2.990(3) | 156 | $1/2-x, 1/2+y, 5/2-z$ |
| N1—H1B...O3 | 0.89 | 2.25 | 3.041(3) | 148 | $1/2-x, -1/2+y, 5/2-z$ |
| O2—H2B...N3 | 0.83 | 1.83 | 2.613(3) | 157 | $1/2-x, -3/2+y, 3/2-z$ |
| O4—H4B...N2 | 0.83 | 1.81 | 2.640(3) | 173 | |
| C11—H11A...O1 | 0.93 | 2.58 | 3.223(3) | 126 | $1/2-x, 3/2+y, 3/2-z$ |
| C18—H18A...O2 | 0.93 | 2.54 | 3.339(4) | 145 | $1/2-x, 1/2+y, 3/2-z$ |
| C19—H19A...O3 | 0.93 | 2.60 | 3.245(3) | 127 | |

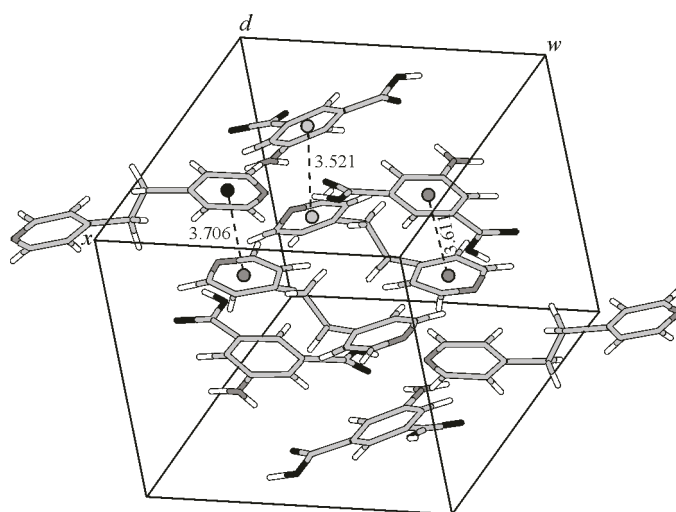


Fig. 4. Fragment of the structure of the title compound that illustrates the $\pi \cdots \pi$ interactions

Table 5

Parameters of $\pi \cdots \pi$ interactions for title compound (\AA , deg.)

| Cg(I) | Cg(J) | Cg \cdots Cg | Perpendicular distance | Dihedral angles | Symmetry operations |
|-------|-------|----------------|------------------------|-----------------|-------------------------|
| Cg(1) | Cg(2) | 3.652 | 3.7057(18) | 4.52(15) | $1/2-x, -1/2+y, 3/2-z$ |
| Cg(1) | Cg(3) | 3.415 | 3.6107(16) | 9.47(13) | $-x, 1-y, 2-z$ |
| Cg(2) | Cg(3) | 3.442 | 3.5213(16) | 5.37(13) | $-1/2+x, 3/2-y, -1/2+z$ |

Cg(1): N2/C16—C17—C18—C19—C20, Cg(2): N3/C9—C10—C11—C12—C13, Cg(3): C1—C2—C3—C4—C5—C6.

parallel to $[0\ 3\ 0]$. The intermolecular interactions link 5-aminoisophthalic acid molecules with head-to-head N—H \cdots O hydrogen bonds, generating $R_2^2(14)$ [12] centrosymmetric dimers, which are extended head-to-tail *via* N—H \cdots O=C hydrogen bond between the amine and carboxylic groups. The hydrogen bonding interactions (Fig. 2 and Fig. 3) are normal, based on H \cdots A distances of 1.81—2.25 \AA , D \cdots A distances of 2.613(3)—3.041(3) \AA , and bond angles of 100—173° (Table 4) [13].

In the title compound, the Apa molecule has usual geometry. The C—C_(ring), C—C_(carboxyl) bond lengths and CCC_(ring), CCC_(carboxyl) angles fall within 1.387(4)—1.395(3) \AA , 1.213(3)—1.492(4) \AA and 118.48(22)—121.31(24)°, 116.78(23)—116.99(23)° ranges with the average values of 1.390(3) \AA , 1.353(3) \AA , and 120.00(13)°, 116.89(23)°. There is no significant difference between the bond angles at the carbon atoms bearing the carboxylic groups and those at the rest of the carbon atoms. The former vary within 120.06—120.97°, and the latter vary within 118.74—121.31° with the average values of 120.52° and 120.16°, the difference being only 0.46°. Both carboxylic groups are nearly coplanar with the aryl ring, as indicated by the torsion angles C3—C8—O3—O4 and C5—C7—O1—O2 of 1.67(35) and $-6.49(47)$ °, respectively [14].

The stability of the structure is additionally reinforced by $\pi \cdots \pi$ interactions of the 1,2-bis(4-pyridyl)ethane molecule with the centroid of the benzene ring of the 5-aminoisophthalic acid molecule with the distances between Cg1 \cdots Cg2 being 3.7057(18) \AA , Cg1 \cdots Cg3 being 3.6107(16) \AA , Cg2 \cdots Cg3 being 3.5213(16) \AA . The dihedral angles between the two rings are 4.52(15)°, 9.47(13)° and 5.37(13)°, respectively (Fig. 4 and Table 5). The stacks are joined into a 3D architecture by O—H \cdots N and N—H \cdots O hydrogen bonds, and by weak C—H \cdots O hydrogen bonds and $\pi \cdots \pi$ stacking interactions [15, 16]. The packing of the molecules in the structure is illustrated in Fig. 5.

CONCLUSIONS

In this study, 1,2-bis(4-pyridyl)ethane and 5-aminoisophthalic acid have been used to construct supramolecular architectures based on crystal engineering principles. It has been observed that supramolecular hydrogen-bonded polymers are formed through self-assembly via O—H \cdots N, O—H \cdots O or C—H \cdots O hydrogen bonding between 1,2-bis(4-pyridyl)ethane and 5-aminoisophthalic acid molecules. The conformations of bipyridines play an important role in the design and construction of desirable frameworks. The change of length, symmetry, and flexibility of the bipyridines could result in a class of materials containing diverse architectures and some related experiments are in progress.

Acknowledgments. This work was financial supported by Yuanpei University, Taiwan.

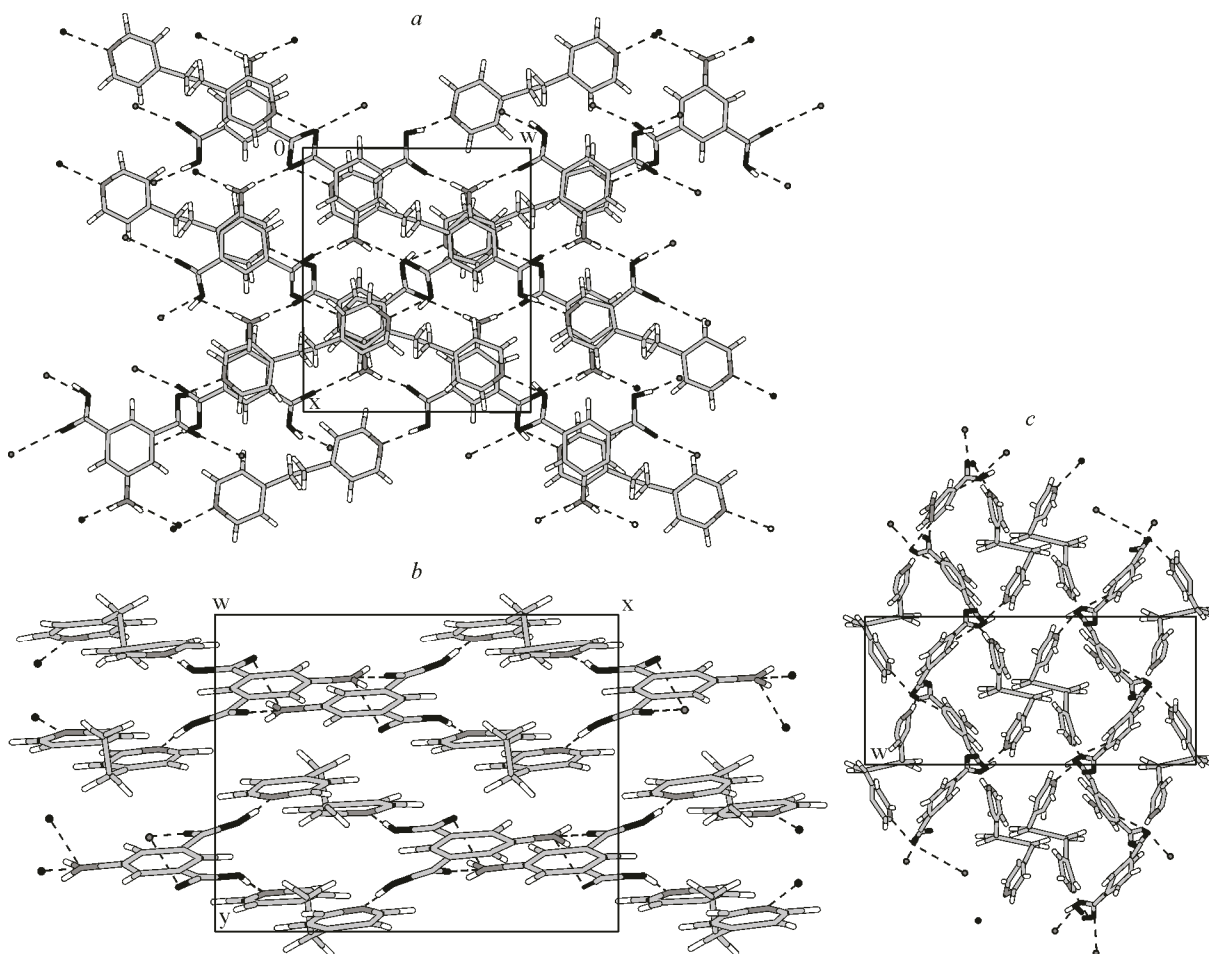


Fig. 5. Packing of the molecules in the title crystal: viewed along the *a* axis (a), viewed along the *b* axis (b), viewed along the *c* axis (c). Dashed lines denote hydrogen bonds

REFERENCES

1. Broker G.A., Tiekink E.R.T. // *CrystEngComm*. – 2007. – **9**. – P. 1096 – 1109.
2. Ebenezer S., Muthiah P.T. // *J. Mol. Struct.* – 2011. – **990**. – P. 281 – 289.
3. Bowes K.F., Ferguson G., Lough A.J., Glidewell C. // *Acta Crystallogr.* – 2003. – **B59**. – P. 100 – 117.
4. Ferguson G., Glidewell C., Gregson R.M., Lavender E.S. // *Acta Crystallogr.* – 1999. – **B55**. – P. 573 – 590.
5. Smith G., Wermuth U.D., White J.M. // *Acta Crystallogr.* – 2005. – **E61**. – P. o313 – o316.
6. Weyna D.R., Shattock T., Vishweshwar P., Zaworotko M.J. // *Cryst. Growth Des.* – 2009. – **9**. – P. 1106 – 1123.
7. Shattock T.R., Arora K.K., Vishweshwar P., Zaworotko M.J. // *Cryst. Growth Des.* – 2008. – **8**. – P. 4533 – 4545.
8. Garcia H.C., Cunha R.T., Diniz R., de Oliveira L.F.C. // *J. Mol. Struct.* – 2012. – **1010**. – P. 104 – 110.
9. Shen F.M., Lush S.F. // *Acta Crystallogr.* – 2010. – **E66**. – P. o1138.
10. Lush S.F., Chen C.W., Yang C., Shen F.M. // *Acta Crystallogr.* – 2011. – **E67**. – P. o652.
11. Sheldrick G.M. // *Acta Crystallogr.* – 2008. – **A64**. – P. 112 – 122.
12. Etter M.C., MacDonald J.C., Bernstein J. // *Acta Crystallogr.* – 1990. – **B46**. – P. 256 – 262.
13. Steiner T. // *Angew. Chem. Int. Ed.* – 2002. – **41**. – P. 48 – 76.
14. Polyanskaya T.M., Smolentsev A.I. // *J. Struct. Chem.* – 2012. – **55**, N 3. – P. 568 – 573.
15. Steiner T. // *Cryst. Rev.* – 1996. – **6**. – P. 1 – 51.
16. Meyer E.A., Castellano R.K., Diederich F. // *Angew. Chem. Int. Ed.* – 2003. – **42**. – P. 1210 – 1250.