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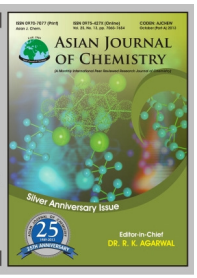


# Tetramer Crystal Structure of Thiophene-2-carboxylic Acid

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The structure of thiophene-2-carboxylic acid (m.f. $C_{20}H_{16}O_8S_4$) was studied by X-ray diffraction. The crystals are orthorhombic, space group $Pna_2(1)$ with a = 10.106(2), b = 14.299(3), c = 16.092(3) Å, α = 90.00, β = 90, γ = 90.00º, V = 2325.5(8) Å$^3$, Z = 4, F(000) = 1056, $D_c$ = 1.464 g/cm$^3$, μ = 0.452 cm$^{-1}$, the final R = 0.0481 and wR = 0.1358. A total of 16217 reflections were collected, of which 3849 were independent ($R_{int}$ = 0.0429).

**Key Words: Tetramer, Crystal structure, Thiophene-2-carboxylic acid.**

## INTRODUCTION

In recent years, heterocyclic compounds had received considerable attentions because of their important biological activity[1]. So the synthesis of broader spectrum and highly bioactive heterocyclic compounds becomes the mainstream in the medicinal and agriculture chemistry field[2]. Thiophene derivatives also exhibited excellent property, such as potential cholinesterase inhibitor[3], antifungal activity[4], antimicrobial activities[5], cytotoxic activity[6], anti HCV activity[7], antiproliferative agents[8].

Nardelli and co-workers[9] obtained the crystal of thiophene-2-carboxylic acid, which is found to be monomer. But in this paper, we reported a tetramer crystal structure of thiophene-2-carboxylic acid, which is linked by O-H-O. The crystal structure was discussed in this paper.

## EXPERIMENTAL

**Crystal structure determination:** The crystal of thiophene-2-carboxylic acid with dimensions of 0.1 2mm × 0.08 mm × 0.06 mm was mounted on a Brucker SMART CCD area-detector diffractometer with a graphite-monochromated $MoK_\alpha$ radiation (λ = 0.71073 Å) by using a phi and scan modes at 113(2) K in the range of 1.91º ≤ θ ≤ 25.02º. The crystal belongs to orthorhombic system with space group $Pna_2(1)$ and crystal parameters of a = 10.106(2) Å, b = 14.299(3) Å, c = 16.092(3) Å, α = 90º, β = 90º, γ = 90º, V = 2325.5(8) A$^3$ $D_c$ = 1.464 g/cm$^3$ The absorption coefficient μ = 0.452 mm$^{-1}$ and Z = 4. The structure was solved by direct methods with SHELXS-97 and refined by the full-matrix least squares method on F$^2$ data using SHELXL-97. The empirical absorption corrections were applied to all intensity data. H atom of N-H was initially located in a difference Fourier map and were refined with the restraint Uiso(H) = 1.2 Ueq(N). Other H atoms were positioned geometrically and refined using a riding model, with d(C-H) = 0.93-0.97 Å and Uiso(H) = 1.2Ueq(C) or 1.5Ueq(C methyl). The final full-matrix least squares refinement gave R = 0.0481 and wR = 0.1358.

## RESULTS AND DISCUSSION

**Structure of thiophene-2-carboxylic acid:** Crystallographic and refinement parameters are given in Table-1. The selected bond lengths and bond angles listed in Tables 2 and 3, respectively. The structure was solved by direct methods. Anisotropic displacement parameters were applied to all nonhydrogen atoms in full-matrix least-square refinements based on F$^2$. The hydrogen atoms were set in calculated positions with a common fixed isotropic thermal parameter. The intermolecular hydrogen bonds are shown in Table-4.

The molecular structure and atom labels are shown in Fig. 1. The one-dimensional line work of hydrogen bonds (dashed lines) is illustrated in Fig. 2, respectively.

Thiophene-2-carboxylic acid crystallizes in the orthorhombic space group $Pna_2(1)$. As can be seen in Fig. 1, the unit cell contains four molecule of thiophene-2-carboxylic acid. The four thiophene rings (C2, C3, C4, C5, S1), (C7, C8, C9, C10, S2), (C12, C13, C14, C15, S3) and (C17, C18, C19, C20, S4) are fairly planar with plane equation 1.491x + (-9.227)y + 12.063z = 1.8131, -0.290x + (-9.254)y + 12.260z = 4.7431,

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR THE TITLE COMPOUND

| Items | Values |
|---|---|
| Empirical formula | $C_{20}H_{16}O_8S_4$ |
| Formula weight | 512.57 |
| Crystal system | Orthorhombic |
| space group | $Pna_2(1)$ |
| Unit cell dimensions | |
| a (Å) | 10.106(2) |
| b (Å) | 14.299(3) |
| c (Å) | 16.092(3) |
| Unit cell angles (º) | |
| α | 90 |
| β | 90 |
| γ | 90 |
| Volume ($Å^3$) | 2325.5(8) |
| Z | 4 |
| Temperature (K) | 113(2) |
| Wavelength (Å) | 0.71073 |
| Calculated density ($g/cm^3$) | 1.464 |
| Absorption coefficient ($mm^{-1}$) | 0.452 |
| $F_{(000)}$ | 1056 |
| Theta range for data collection (º) | 1.91-25.02 |
| Reflections collected | 16217 |
| Independent reflections | 3849 [$R_{(int)}$ = 0.0429] |
| Final R indices [I > 2σ(I)] | $R_1$ = 0.0481, $wR_2$ = 0.1358 |

TABLE-2
SELECTED BOND LENGTHS [Å] FOR THE TITLE COMPOUND

| Bond lengths | X-Ray crystal | Bond lengths | X-Ray crystal |
|---|---|---|---|
| S(1)-C(5) | 1.717(5) | C(1)-C(2) | 1.471(5) |
| S(1)-C(2) | 1.718(4) | C(2)-C(3) | 1.410(5) |
| S(2)-C(10) | 1.706(4) | C(3)-C(4) | 1.406(6) |
| S(2)-C(7) | 1.726(4) | C(4)-C(5) | 1.344(6) |
| S(3)-C(15) | 1.709(4) | C(6)-C(7) | 1.489(5) |
| S(3)-C(12) | 1.712(4) | C(7)-C(8) | 1.412(5) |
| S(4)-C(20) | 1.713(5) | C(8)-C(9) | 1.427(6) |
| S(4)-C(17) | 1.716(4) | C(9)-C(10) | 1.371(5) |
| O(1)-C(1) | 1.246(4) | C(11)-C(12) | 1.487(5) |
| O(2)-C(1) | 1.339(5) | C(12)-C(13) | 1.365(5) |
| O(3)-C(6) | 1.250(4) | C(13)-C(14) | 1.434(6) |
| O(4)-C(6) | 1.328(4) | C(14)-C(15) | 1.335(6) |
| O(5)-C(11) | 1.250(4) | C(16)-C(17) | 1.471(5) |
| O(6)-C(11) | 1.330(5) | C(17)-C(18) | 1.374(6) |
| O(7)-C(16) | 1.242(4) | C(18)-C(19) | 1.432(6) |
| O(8)-C(16) | 1.346(5) | C(19)-C(20) | 1.344(6) |

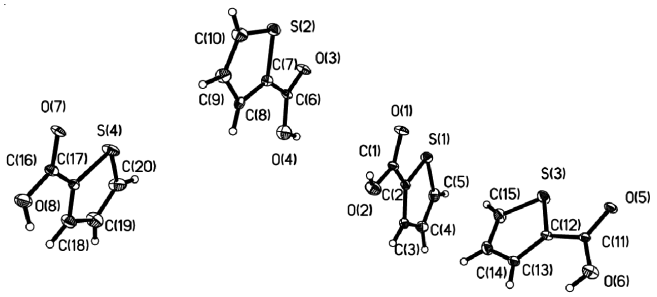


Fig. 1. Molecular Structure of the title compound

-2.221x + 6.595y + 13.834z = 2.8185 and -1.109x + (-7.032)y + 13.900z = 8.9486, respectively[5] and the largest deviation from the least squares plane is 0.0024 Å[6]. Meanwhile, the first thiophene ring is vertically with the third thiophene ring with the dihedral angles of 71.7º and is parallel with the second ring and four ring with the dihedral angles of 10.1, 18.4º, respectively.

TABLE-3
SELECTED BOND ANGLES [º] FOR THE TITLE COMPOUND

| Bond angles | X-Ray crystal | Bond angles | X-Ray crystal |
|---|---|---|---|
| C(5)-S(1)-C(2) | 92.1(2) | C(9)-C(10)-S(2) | 112.1(3) |
| C(10)-S(2)-C(7) | 91.7(2) | O(5)-C(11)-O(6) | 121.9(4) |
| C(15)-S(3)-C(12) | 91.29(19) | O(5)-C(11)-C(12) | 119.8(3) |
| C(20)-S(4)-C(17) | 91.8(2) | O(6)-C(11)-C(12) | 118.3(3) |
| O(1)-C(1)-C(2) | 119.8(3) | C(13)-C(12)-C(11) | 129.6(3) |
| O(2)-C(1)-C(2) | 117.3(3) | C(13)-C(12)-S(3) | 111.8(3) |
| C(3)-C(2)-C(1) | 130.8(3) | C(11)-C(12)-S(3) | 118.6(3) |
| C(3)-C(2)-S(1) | 110.9(3) | C(12)-C(13)-C(14) | 111.6(3) |
| C(1)-C(2)-S(1) | 118.2(3) | C(15)-C(14)-C(13) | 112.4(4) |
| C(4)-C(3)-C(2) | 110.7(3) | C(14)-C(15)-S(3) | 112.8(3) |
| C(5)-C(4)-C(3) | 114.9(4) | O(7)-C(16)-O(8) | 122.0(4) |
| C(4)-C(5)-S(1) | 111.4(3) | O(7)-C(16)-C(17) | 120.0(3) |
| O(3)-C(6)-O(4) | 123.8(4) | O(8)-C(16)-C(17) | 118.0(3) |
| O(3)-C(6)-C(7) | 119.9(3) | C(18)-C(17)-C(16) | 130.6(3) |
| O(4)-C(6)-C(7) | 116.4(3) | C(18)-C(17)-S(4) | 110.9(3) |
| C(8)-C(7)-C(6) | 129.2(3) | C(16)-C(17)-S(4) | 118.5(3) |
| C(8)-C(7)-S(2) | 112.4(3) | C(17)-C(18)-C(19) | 112.6(4) |
| C(6)-C(7)-S(2) | 118.3(3) | C(20)-C(19)-C(18) | 111.9(4) |
| C(7)-C(8)-C(9) | 109.6(3) | C(19)-C(20)-S(4) | 112.8(4) |
| C(10)-C(9)-C(8) | 114.1(4) | | |

TABLE-4
HYDROGEN BOND LENGTHS (Å) AND BOND ANGLES (°)

| D-H···A | d(D-H) | d(H···A) | d(D···A) | ∠DHA |
|---|---|---|---|---|
| O(2)-H(2)...O(5)#1 | 0.82 | 2.12 | 2.936(4) | 172.1 |
| O(4)-H(4)...O(7)#2 | 0.82 | 2.10 | 2.885(4) | 161.0 |
| O(6)-H(6)...O(7)#3 | 0.82 | 2.18 | 2.918(4) | 149.0 |
| O(8)-H(8)...O(5)#4 | 0.82 | 2.17 | 2.828(4) | 136.7 |

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,z+1/2 #2 -x+1/2,y-1/2,z-1/2 #3 x,y,z-1. #4 x+1,y,z+1.

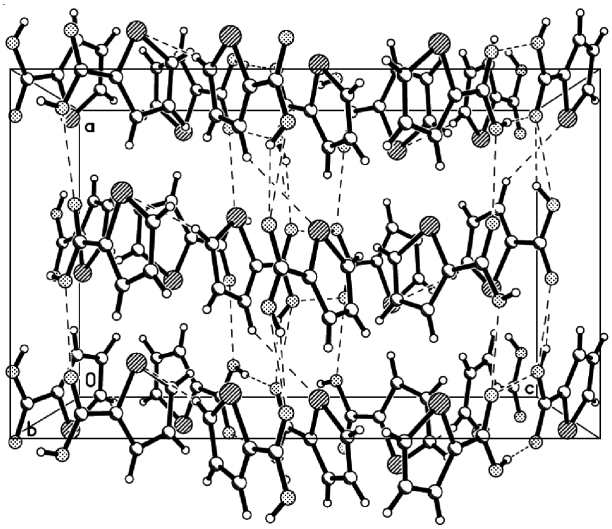


Fig. 2. Two-dimensional network of hydrogen bonds (dashed lines)

In Table-2, the results indicate that the lengths of three C-S bond C5-S1, C7-S2, C12-S3 and C17-S4 are 1.718(4)Å, 1.726(4)Å, 1.712(4) Å and 1.716(4) Å, respectively, which are the same with that in the single heterocycle ring. Also, the C1-O1, C6-O3, C11-O5 and C17-O7 are same as the general C=O double bond length. From the Table-3, all of the angle of thiophene and carboxylic acid are ranged in normal range.

As shown in Fig. 2, hydrogen-bonding interactions stabilize the solid state of the crystal structure in the crystal packing. The title compound has an extensive network of hydrogen bonding involving the two acceptor atoms O (Table-4). In the ac plane, they are linked together by O(2)-H(2)...O(5)#1, O(4)-H(4)...O(7)#2, O(6)-H(6)...O(7)#3, O(8)-H(8)...O(5)#4 hydrogen bonds. This hydrogen-bonding sequence is repeated to form a ring and line. The ring has four O atoms at the vertices, leading to a hydrogen-bond network defining cyclic motifs denoted $R_2^2$ (8).

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