Self-assembly of 4-Methyl-benzoic Acid Ethyl Ester Assisted by C—H···O Hydrogen Bonds*

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Abstract: 4-Methyl-benzoic acid ethyl ester [$C_{10}H_{12}O_2$] was obtained by crystallization of 4-methyl-benzoic acid in ethanol hot solution, and structurally characterized by single-crystal X-ray crystallography, and the crystal is of monoclinic, space group $P2_{1/c}$ with a=11.798 (1), b=13.209 (1), c=1.160 0 (1) nm, β=107.706 (2)°, V=1.721 9 (3) nm^3, $C_{10}H_{12}O_2$, M_r=164.20, D_c=1.267 g/cm^3, Z=8, F (000) =704, μ (MoKα) =0.087 cm^{-1}, R=0.084 1 and wR=0.278 9. The total reflections were 8 557 and 3 027 were independent of which 1 902 were observed with $I>2\sigma(I)$. The title compound $C_{10}H_{12}O_2$ are connected by C—H···O hydrogen bonds between methyl groups and carbonyl oxygen atoms from adjacent molecules to form a 1D chain.

Key words: self-assembly; C—H···O hydrogen bonds; 4-methyl-benzoic acid ethyl ester

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Intermolecular interactions play an important role in the formation of stable supramolecular structure[1—3]. C—H···O hydrogen bonds are known driving forces which direct molecular aggregation in organic crystals[4—5] and may be used to design specific architecture with intent to realize specific chemical and physical properties[6—7]. In this text oxygen atom is a good hydrogen bond acceptor. Oxygen··· phenyl oxygen··· naphthyl and oxygen··· pyridyl synthons have been identified in some of crystal structures and to influence overall crystal packing[6, 8—11]. Esterifying reactions are often carried out under acid catalysis. We designed the reaction of melamine and trimellitic acid under reflux in methanol solution resulting in esterification of the 1-carboxylic group of trimellitic acid in a high yield[9], this work has provided us an inspiration for the usage of crystallization of carboxylic acid in hot ethanol solution to obtain ester. Thus we carried out crystallization of 4-methyl-benzoic acid from ethanol as it can form the corresponding ester very easily. Our approach is to expose the ease of synthesis of such ester as the conventional methods often have limitations due to complex procedures involving acid catalysis and reflux. In this paper we report and discuss the crystal structure of 4-methyl-benzoic acid ethyl ester.

1 Experiment

1.1 Synthesis

4-methyl-benzoic acid (0.164 g 1 mmol) was added to hot ethnanol (15 mL) with stirring for 2 h. The filtrate was allowed to stand at room temperature for 1 week. Colorless plate crystals of the title compound suitable for X-ray analysis were obtained by slow evaporation. Anal. Calcd. (w/%) for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37; O, 19.49. Found (w/%): C, 73.08; H, 7.29; O, 19.41. IR (ν/cm^{-1}, KBr): 3 078 w, 2 953m, 1 732m, 1 664vs 1 514m, 1 375m, 1 468w, 1 278w, 1 190w.

1.2 Structure determination and refinement

A crystal of the title compound with approximate dimensions of 0.35 mm×0.28 mm×0.16 mm was mounted on a glass fiber. Data collections were made on a Bruker SMART Apex CCD diffractometer equipped with a graphite-monochromatized MoKα radiation (λ=0.071 073 nm) at 293 (2) K. The data sets were corrected by SADABS program. A total of 8557 reflections were collected in the range of $1.81°<\theta<25.00°$, of which 3027 were independent and 1902 with $I>2\sigma(I)$ were considered as observed and used in the structure determination and refinement. The structure was charaterized by direct methods using SHELXTL[12]. All of the non-H atoms were refined anisotropically, and hydrogen atoms were placed in the

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geometrically calculated positions. The final refinement by full-matrix least-squares were converged to R = 0.084 1 and wR = 0.278 9 ($w = 1/[\sigma^2(F_o^2) + (0.1790P)^2 + 0.5845P]$, where $P = (F_o^2 + 2F_c^2)/3$). S = 1.084, $(\Delta/\sigma)_{max} = 0.000$, $(\Delta\rho)_{max} = 0.630$ and $(\Delta\rho)_{min} = -0.370$ e/Å. The structural plots were drawn with SHELXTL.

2 Results and discussion

Single crystal of 4-methyl-benzoic acid ethyl ester was obtained upon crystallization from hot a ethanol solution to provide an easy approach of synthesis of such ester under mild reaction condition. The nature of its self-assembly was investigated using single crystal X-ray diffraction analysis. The result showed a monoclinic crystal lattice with a $P2_{1/c}$ space group. The compound gave an asymmetric unit with two symmetry-independent molecules. At the beginning, the two symmetry-independent molecules (A and B) are approximately coplanar [dihedral angle 10.7°] (Fig.1).

The hydrogen atom on the methyl group serves as the donor and carbonyl oxygen atom behaves as the acceptor. The quite exotic features of the packing of the molecules was revealed by the analysis of molecular arrangement in the crystal lattice. The C—H··· O interactions serve as the structure directing factor. Inversion related sym metry-independent A molecules or B molecules are linked through C—H··· O (C··· O, 0.268 5 (4) nm, 156.0°; 0.268 5 (6) nm, 171.8°) hydrogen bonds involving methyl group and carbonyl oxygen to form infinite zigzag chain [$C_{10}H_{12}O_2$] along b axis.

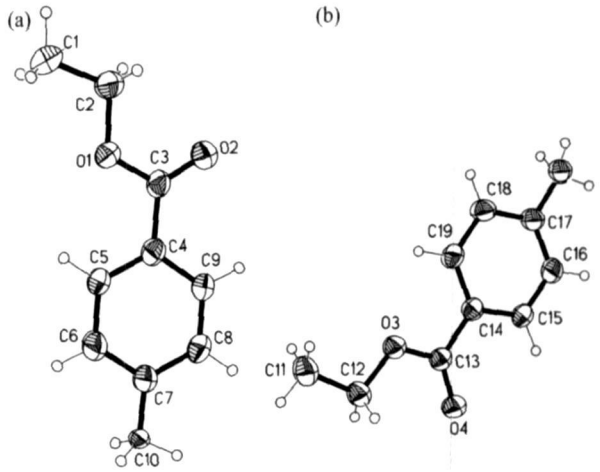

Fig.1 Molecular structure of $C_{10}H_{12}O_2$ (30% probability thermal ellipsoids)

In each chain, the adjacent molecules are held together by C—H··· O hydrogen bonds with the chains from molecules A and the chains from molecules B arranging alternately along c axis forming a sheet parallel to the crystallographic (101) plane. It is worth noting that C—H··· O bonds are unusual short distance (C··· O, 0.268 5 (4) nm), which are shorter than the usual 0.290 nm of strong N—H··· O (hydrogen bonds[11], in contrast to the distance of charge-assistant N^+—H··· O^- (0.265 4 (3) nm)[8], N^+—H··· O (0.266 2 (4)[9], 0.267 ~ 0.272 nm[13]) hydrogen bonds known in the literatures. It is possible due to inductive effects of a para methyl substituent which results in oxygen atom of carbonyl gains a slightly negative charge and the hydrogen atom of methyl group gains a slightly

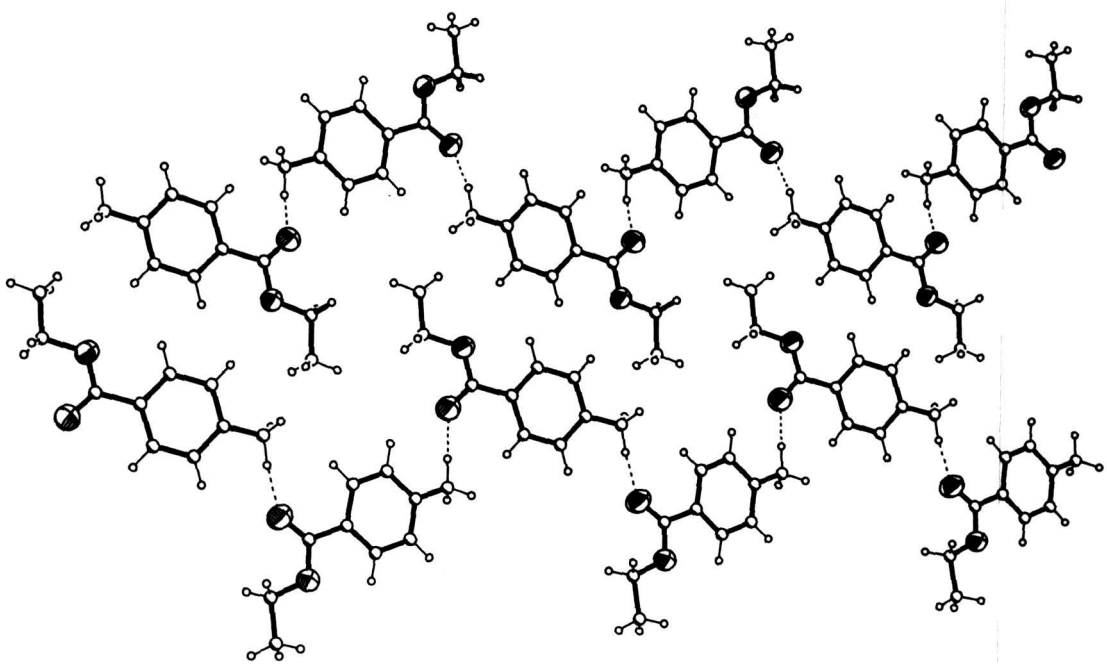

Fig.2 Zigzag chains built from two symmetry-independent molecules (A and B) via C—H··· O hydrogen bonds

positive charge. This is an additional strong hydrogen bonding effect. There is no π—π stacking interaction in the structure. The adjacent chains built from molecules A and chains built from molecules B adopt a close packing arrangement. It indicates that weak C—H···O interactions may direct self-assembly of supramolecular architectures as N—H···O hydrogen bonds leading to the creation of a range of supramolecular recognitions.

Tab.1　Selected bond lengths and angles of the title compound

Bond	Length/nm	Bond	Length/nm	Bond	Length/nm
O(1)—C(3)	0.131 9(4)	C(4)—C(5)	0.137 5(5)	C(13)—C(14)	0.148 1(5)
O(1)—C(2)	0.147 3(5)	C(4)—C(9)	0.138 7(5)	C(14)—C(19)	0.137 5(5)
O(2)—C(3)	0.122 4(4)	C(5)—C(6)	0.138 4(6)	C(14)—C(15)	0.138 8(5)
O(3)—C(13)	0.132 1(4)	C(6)—C(7)	0.137 3(5)	C(15)—C(16)	0.138 3(5)
O(3)—C(12)	0.145 0(4)	C(7)—C(10)	0.133 9(5)	C(16)—C(17)	0.135 6(5)
O(4)—C(13)	0.121 9(4)	C(7)—C(8)	0.138 6(6)	C(17)—C(20)	0.135 6(5)
C(1)—C(2)	0.146 6(6)	C(8)—C(9)	0.136 1(6)	C(17)—C(18)	0.138 4(5)
C(3)—C(4)	0.147 2(5)	C(11)—C(12)	0.147 8(6)	C(18)—C(19)	0.139 4(5)
Bond	**Angle/(°)**	**Bond**	**Angle/(°)**	**Bond**	**Angle/(°)**
C(3)—O(1)—C(2)	117.1(3)	C(6)—C(7)—C(8)	119.4(4)	C(20)—C(17)—C(18)	116.8(3)
C(7)—C(6)—C(5)	119.6(4)	C(17)—C(16)—C(15)	120.1(3)	C(5)—C(4)—C(3)	121.7(3)
C(19)—C(14)—C(13)	121.2(3)	O(2)—C(3)—C(4)	124.6(3)	O(4)—C(13)—O(14)	124.5(3)
C(13)—O(3)—C(12)	117.7(3)	C(9)—C(8)—C(7)	120.6(3)	C(17)—C(18)—C(19)	118.9(4)
C(10)—C(7)—C(6)	118.4(4)	C(16)—C(17)—C(20)	122.2(3)	C(9)—C(4)—C(3)	119.9(3)
C(15)—C(14)—C(13)	119.7(3)	O(1)—C(3)—C(4)	113.9(3)	O(3)—C(13)—O(14)	113.4(3)
C(1)—C(2)—O(1)	108.2(4)	C(8)—C(9)—C(4)	120.8(4)	C(14)—C(19)—C(18)	120.6(3)
C(10)—C(7)—C(8)	122.2(4)	C(16)—C(17)—C(18)	120.9(4)	C(4)—C(5)—C(6)	121.3(4)
C(16)—C(15)—C(14)	120.4(3)	C(5)—C(4)—C(9)	118.3(4)	C(19)—C(14)—C(15)	119.1(3)
O(2)—C(3)—O(1)	121.5(4)	O(3)—C(12—O(11)	108.4(3)		

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4-甲基苯甲酸乙酯中的 C—H…O氢键自组装

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摘 要: 4-甲基苯甲酸乙酯由 4-甲基苯甲酸在热的乙醇溶液中酯化获得, 在室温下缓慢蒸发溶剂得到晶体。用元素分析、IR、X射线单晶衍射分析进行了结构表征。结构分析表明, 晶体属单斜晶系, $P2_{1/c}$空间群, $a = 1.179\,8(1)$ nm, $b = 1.320\,9(1)$ nm, $c = 1.160\,0(1)$ nm, $\beta = 107.706(2)^\circ$, $V = 1.721\,9(3)$ nm^3, $Z = 8$, $\rho = 1.267$ g/cm^3, $C_{10}H_{12}O_2$, $M_r = 164.20$, $F(000) = 704$, $\mu(MoK\alpha) = 0.87$ mm^{-1}, $R = 0.084\,1$和 $wR = 0.2789$。总衍射点 8 557个, 独立衍射点 3 027个, 可观察点 1 902个, 满足 $I > 2\sigma(I)$。通过甲基与相邻分子的羰基之间的 C—H…O氢键将 4-甲基苯甲酸乙酯分子沿 b轴方向组装成一维 Z字超分子链。

关键词: 自组装; C—H…O; 氢键; 4-甲基苯甲酸乙酯
中图分类号: O631

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沉降速率系数确定方法

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摘 要: 沉降速率法常用于确定路面施工时机, 因此沉降速率系数的确定对路面施工非常重要。当路基的地质、地基处理、施工等方面的资料都齐全时, 可以按照固结理论计算得到沉降速率系数。在工程实践中更多地利用施工监测资料反演计算沉降速率系数, 目前常用的反演方法有三点法、孔压~时间曲线拟和法等。在固结理论等已有研究成果的基础上提出了 $t\sim 1nS_r$法、$S_t\sim V_s$法、双曲线法、Asaoka法等方法, 工程实践证明上述方法是可行的。理论分析和工程实践都表明多层地基的沉降速率系数随时间增加而减小。

关键词: 沉降速率法; 沉降速率系数; 反演; 多层地基
中图分类号: U416