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RESEARCH ARTICLE

YANG Yuan, ZHANG Jinnan, LUO Surong, SONG Xiaohong, LI Qi

Synthesis and crystal structure of inclusion compounds: *Trans*-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid with boric acid and tetrabutylammonium salt

Abstract Two new inclusion compounds $(n\text{-}C_4H_9)_4N^+C_{18}H_{13}O_4^- \cdot B(OH)_3$ (**1**) and $(n\text{-}C_4H_9)_4N^+C_{18}H_{13}O_4^-$ (**2**) were prepared and characterized by X-ray crystallography. Crystal data: compound 1, monoclinic $P2(1)/c$, $a = 1.569\ 9(1)$ nm, $b = 0.995\ 5(6)$ nm, $c = 2.293\ 3(1)$ nm, $\beta = 109.962(3)°$, $Z = 4$, and $R_1 = 0.0434$, $wR = 0.075\ 9$; compound **2**, monoclinic $C2/c$, $a = 1.400\ 5(3)$ nm, $b = 1.282\ 1(2)$ nm, $c = 1.765\ 7(3)$ nm, $\beta = 100.388(1)°$, $Z = 4$, and $R_1 = 0.0584$, $wR = 0.096\ 6$. In the crystal structure of 1, the tetramers formed by two *trans*-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid (EADA) anions and two boric acid molecules were connected through O—H···O hydrogen bonds to generate a channel type host lattice. The tetra-*n*-butylammonium cations were stacked to give two columns within each channel with cross-sectional size of about 2.30 nm × 0.93 nm. In the crystal structure of 2, similar honeycomb host lattices with big size were also formed along the [101] direction by three-dimensional accumulation of EADA anions. The tetra-*n*-butylammonium cations were accommodated in a zigzag fashion within each channel.

Keywords *Trans*-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid, boric acid, tetra-*n*-butylammonium salt, inclusion compound, crystal structure

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YANG Yuan, LUO Surong, LI Qi (✉)
College of Chemistry, Beijing Normal University, Beijing 100875, China
E-mail: qili@bnu.edu.cn

ZHANG Jinnan, SONG Xiaohong
School of Chemical Biology and Pharmaceutical Sciences, Capital University of Medical Sciences, Beijing 100054, China

LUO Surong
The High School Affiliated to Beijing Youth Politics College, Beijing 100015, China

1 Introduction

Hydrogen bonds continue to attract scientists' interest due to their extreme importance in nature [1]. The specificity and the widespread occurrence of hydrogen bonds make them a special construction element in crystal engineering [2]. The main emphasis in crystal engineering is to design novel materials with precise topological control generated through intermolecular interactions. The packings of molecules in crystalline solids through hydrogen bonded tapes, ribbons, and other motifs have demonstrated the use of functional groups in molecules [3,4]. "Coordinatoclathrate", the design principle for a new host type, developed by Weber *etc*. [5], is a new host type with both a bulky rigid skeleton and suitably positioned functional groups such as carboxyl, hydroxyl, amido groups, and the ones with lone pairs of electrons, all of which are easy to develop hydrogen bonds. Therefore, it is a specific combination of topological and coordinative host-guest interactions in the solid state [6].

Trans-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid (EADA) (Fig. 1) with both a bulky basic V-shape molecular skeleton and appended suitably positioned carboxylic functional groups which provide hydrogen bonding to guests or to other host molecules has been intensively studied and proved to be an efficient clathrate host molecule. The EADA in the form of a H-bonded dimer through a pair of O—H···O hydrogen bonds between their carboxyl groups has been reported [6]. Each dimer is then H-bonded to two other centrosymmetrically related dimmers through its two exocarboxyl groups. In this way the three $R_2^2(8)$ rings with different sizes and areas are generated and EADA are linked to form infinite broad zigzag chains. Un-closed nano channel host lattices with guest molecules occupying the intervening space are assembled by these isolated zigzag chains. There are no direct host-guest H-bonds between the host and guest molecules in the structures. Therefore, instead of coordinatoclathrates true clathrates are formed, indicating the strong tendency of host compound EADA towards homodimerization [7]. 9,10-Dihydro-9,10-ethanoanthracene-11,12-dicarboxamide has been proved to make accessible new crystalline inclusions with hydrogen bond interactions between the host and guest molecules [8].

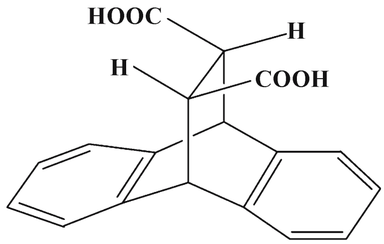

Fig. 1 Host molecule EADA

Different inclusion compounds can be obtained even with the same host and guest molecules. It has been revealed that racemic EADA [9] and (S,S)-(-)-EADA [10] show similar inclusion property but they form two different inclusion crystals with acetic acid. The first one crystallizes in $P21/n$ space group and the guest acetic acid molecules form non-planar dimers through O—H···O hydrogen bonds. The dimers lie in the channels made by the host molecules. However, the second one's space group is $P4_3$. The host EADA molecules are linked through hydrogen bonds forming four fold helix chains in the direction of [001]. Thus the host molecules enwrap the guest dimers in a helical way, forming a helical inclusion compound which rarely appears in organic inclusion crystals. At $T = 278$ K, acetic acid, water, and EADA crystallize, giving an inclusion compound, in which the two acetic acid molecules and two water molecules form a tetramer that perform as the guest molecule [7].

In recent years, we have done a systematic study on the generation of new urea/thiourea/selenourea-anion inclusion complexes and the hydrogen-bonding patterns in their crystal structures. Our research results demonstrate that novel inclusions possess all kinds of inclusion types due to the use of different components [11−15]. A great number of novel inclusion compounds have been synthesized using multi-carboxyl aliphatic or aromatic ring molecules, with or without urea/thiourea molecules [16,17]. As part of our ongoing investigation of the properties and molecular packing of inclusions, we report herewith the preparation and X-ray crystallographic analysis of a pair of crystalline inclusion compounds of tetra-*n*-butylammonium with the host lattice built of boric acid and EADA, $(n\text{-}C_4H_9)_4N^+C_{18}H_{13}O_4^- \cdot B(OH)_3$ (**1**), and the one built of EADA alone, $(n\text{-}C_4H_9)_4N^+C_{18}H_{13}O_4^-$(**2**), respectively.

2 Experimental

2.1 Reagents and instruments

The EADA was synthesized by Diels-Alder reaction of anthracene with fumaric acid [18]. Anthracene (chemical purity) was obtained from Beijing Chemical Reagent Company and fumaric acid (analytical purity) was obtained from Beijing Jinlong Chemical Reagent Company. Tetra-*n*-butylammonium hydroxide (25 wt% aqueous solution, chemical purity) was obtained from Beijing Fubide Fine Chemical Co., Ltd. Boric acid (analytical purity) was obtained from Tianjin No. 3 Chemical Reagent Factory.

Infrared spectra were recorded on a NEXUS 670 Fourier transform infrared (FT-IR) spectrophotometer (KBr Disc Technique). Microanalyses were performed on a Vario EL Elemental Analyzer.

2.2 Synthesis

Boric acid, EADA and tetra-*n*-butylammonium hydroxide were mixed in a molar ratio of 1:2:3 for preparation of compound **1**, and EADA and tetra-*n*-butylammonium hydroxide were mixed in a molar ratio of 1:2 for preparation of compound **2**, respectively. The mixtures were dissolved in a minimum amount of acetone, after stirring the mixture for about 30 min, the solution was subjected to slow evaporation at room temperature in a desiccator. Yellowish crystals were obtained about ten days later.

IR υ (cm^{-1}) (1): 3 422.6 (vs), 2 963.8 (s), 2 875.1(m), 1 735.7(s), 1 582.9(vs), 1 482.7(m), 1 460.0(s), 1 383.6(m), 1 255.4(m) cm^{-1}; (2); 3 448.8(vs), 2 961.2(s), 2 866.7(m), 1 636.8(vs), 1 479.2(m), 1 384.7(m), 1 258.9(m) cm^{-1}; Anal. calcd for $C_{34}H_{52}O_7BN$ (1): C 68.34, H 8.770, N 2.344; found C 68.04, H 8.547, N 2.300; Anal. calcd for $C_{34}H_{49}O_4N$ (**2**): C 76.22, H 9.219, N 2.615; found C 74.21, H 9.067, N 2.317. Elemental analysis of the inclusion compounds gave the molecular formula $(n\text{-}C_4H_9)_4N^+C_{18}H_{13}O_4^- \cdot B(OH)_3$ (**1**) and $(n\text{-}C_4H_9)_4N^+C_{18}H_{13}O_4^-$ (**2**).

2.3 Crystallography

Intensity data were collected on a Bruker Smart CCD diffractometer (monochromatized Mo $K\alpha$ X-ray source, $\lambda = 0.071\,073$ nm) at 120 K for compound **1** and 293 K for compound **2**, respectively. The structure was solved by the directed method and refined with anisotropic non-hydrogen atoms by full-matrix least squares on F_o^2 using SHELX-97 package [19]. Hydrogen atoms were located geometrically and refined in the rigid-body approximation. In compound **2**, the carboxyl (C (17), O (1), and O (2)) of EADA anions were disordered over two positions with site occupancy factors 0.7 and 0.3 respectively. The disordered atoms were refined with equivalent anisotropic displacement parameters. The final positional and equivalent isotropic thermal parameters of **1** and **2** were listed in Table 1. Selected bond distances (Å), bond angles (°) and hydrogen bonds were given in Table 2 and Table 3, and atom labelings were in accordance with Figs. 2 and 4.

3 Results and discussion

3.1 Infrared spectra

In the IR spectra, peaks at about 1 582.9 (vs) and 1 383.6 (m) cm^{-1} were ascribed to antisymmetric vibration and symmetric

Table 1 Coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (nm$^2 \times 10^5$) of nonhydrogen atoms

Atom	x	y	z	U_{eq}^*	Atom	x	y	z	U_{eq}^*
(n-$C_4H_9)_4N^+C_{18}H_{13}O_4^- \cdot B(OH)_3$ (**1**)									
B(1)	312(1)	−1 816(2)	4 704(1)	25(1)	C(14)	4 045(1)	−3 470(1)	3 446(1)	22(1)
O(1)	−186(1)	−1 800(1)	5 086(1)	35(1)	C(15)	4 546(1)	−2 287(1)	4 622(1)	21(1)
O(2)	495(1)	−3 046(1)	4 522(1)	28(1)	C(16)	3 957(1)	−3 386(1)	4 484(1)	21(1)
O(3)	590(1)	−633(1)	4 522(1)	30(1)	C(17)	3 223(1)	140(1)	3 352(1)	24(1)
O(4)	2 362(1)	557(1)	3 184(1)	27(1)	C(18)	2 009(1)	−2 124(1)	3 831(1)	25(1)
O(5)	3 744(1)	619(1)	3 127(1)	34(1)	N(1)	8 213(1)	4 946(1)	3 810(1)	22(1)
O(6)	1 639(1)	−971(1)	3 800(1)	28(1)	C(19)	7 831(1)	6 064(1)	3 347(1)	27(1)
O(7)	1 743(1)	−3 169(1)	4 011(1)	35(1)	C(20)	8 425(1)	7 288(1)	3 399(1)	29(1)
C(1)	5 237(1)	−2 168(1)	3 283(1)	28(1)	C(21)	7 890(1)	8 375(1)	2 961(1)	36(1)
C(2)	5 312(1)	−3 116(2)	2 859(1)	33(1)	C(22)	8 435(1)	9 654(1)	3 000(1)	48(1)
C(3)	4 763(1)	−4 239(2)	2 736(1)	35(1)	C(23)	7 471(1)	3 896(1)	3 680(1)	27(1)
C(4)	4 123(1)	−4 421(1)	3 023(1)	30(1)	C(24)	7 680(1)	2 687(1)	4 107(1)	30(1)
C(5)	5 098(1)	−2 053(1)	5 225(1)	26(1)	C(25)	6 945(1)	1 621(1)	3 880(1)	33(1)
C(6)	5 072(1)	−2 918(1)	5 695(1)	31(1)	C(26)	7 095(1)	489(2)	4 350(1)	53(1)
C(7)	4 495(1)	−4 009(1)	5 557(1)	30(1)	C(27)	8 479(1)	5 465(1)	4 470(1)	22(1)
C(8)	3 934(1)	−4 241(1)	4 952(1)	26(1)	C(28)	7 782(1)	6 290(1)	4 631(1)	24(1)
C(9)	4 460(1)	−1 430(1)	4 059(1)	22(1)	C(29)	8 110(1)	6 466(1)	5 335(1)	27(1)
C(10)	3 395(1)	−3 500(1)	3 802(1)	22(1)	C(30)	7 574(1)	7 507(1)	5 550(1)	41(1)
C(11)	2 820(1)	−2 198(1)	3 614(1)	21(1)	C(31)	9 078(1)	4 366(1)	3 754(1)	24(1)
C(12)	3 456(1)	−9 59(1)	3 836(1)	21(1)	C(32)	8 999(1)	3 679(1)	3 147(1)	28(1)
C(13)	4 605(1)	−2 344(1)	3 573(1)	23(1)	C(33)	9 917(1)	3 114(1)	3 185(1)	34(1)
C(34)	9 904(1)	2 413(2)	2 594(1)	41(1)					
n-$C_4H_9)_4N^+C_{18}H_{13}O_4^-$ (**2**)									
O(1)	2 940(2)	2 038(2)	2 076(2)	95(1)	C(22)	1 629(3)	835(3)	174(2)	140(2)
O(1A)	3 892(6)	2 105(5)	990(4)	99(2)	C(13)	4 103(2)	−148(2)	2 753(2)	58(1)
O(2)	4 111(2)	3 214(2)	2 398(2)	100(1)	C(14)	4 972(2)	−152(2)	3 288(1)	59(1)
O(2A)	4 627(7)	3 272(5)	1 814(5)	97(3)	C(4)	4 983(3)	−582(2)	4 009(2)	80(1)
N(1)	0	1 336(2)	2 500	59(1)	C(3)	4 149(4)	−1 023(2)	4 182(2)	100(1)
C(27)	788(2)	2 055(2)	2 913(1)	64(1)	C(2)	3 302(3)	−1 029(2)	3 653(2)	97(1)
C(28)	1 655(2)	1 544(2)	3 408(2)	74(1)	C(1)	3 285(2)	−593(2)	2 936(2)	76(1)
C(29)	2 379(2)	2 379(2)	3 746(2)	88(1)	C(9)	4 207(2)	371(2)	1 998(1)	61(1)
C(30)	3 277(2)	1 930(3)	4 246(2)	102(1)	C(12)	4 552(2)	1 513(2)	2 185(2)	66(1)
C(19)	388(2)	625(2)	1 937(2)	68(1)	C(17)	3 798(4)	2 274(3)	2 218(3)	74(1)
C(20)	786(2)	1 143(2)	1 299(2)	81(1)	C(17A)	4 296(8)	2 349(7)	1 621(6)	73(3)
C(21)	1 208(2)	346(3)	822(2)	93(1)					

U_{eq}^* is defined as one third of the trace of the orthogonalized U_{ij} tensor.

vibration absorption of $-COO^-$ in compound **1** [20]. The peak at 1 735.7 (s) cm^{-1} indicated the characteristic of COOH, it was in agreement with the present crystal structure result. A strong band at about 1 460.0 cm^{-1} might be attributable to the asymmetric vibration of B–O of boric acid [21]. Comparing with the IR spectrum of compound **1**, there was only one strong band at about 1 636.8 cm^{-1} for compound **2**, indicating that the two carboxyl groups had the same chemical environment due to ionization of one carboxyl group and formation of intramolecule hydrogen bond between the two carboxyl groups.

3.2 Structure description

3.2.1 Crystal structures of (n-$C_4H_9)_4N^+C_{18}H_{13}O_4^- \cdot B(OH)_3$ (1)

In compound **1**, there were one EADA anion, one boric acid molecule, and one (n-$C_4H_9)_4N^+$ cation in an asymmetric unit. The atoms of phenyl rings of the host molecule showed highly planar property, the dihedral angle between two phenyl rings is 57.6°. It can be seen from Table 2 that there is a distinct difference between the bond lengths of two carboxyls' C–O. The bond length of the hydroxylic oxygen C(17)–O(4) was longer than that of carboxylic oxygen C(17) = O(5). However, the bond lengths of C(18)–O(6) and C(18)–O(7) manifested average effect due to ionization of carboxyl group. In the bridged ethyl, the bond lengths of C(9)–C(12), C(10)–C(11), and C(11)–C(12) were close to each other; the values were 0.155 38(2), 0.155 37(2) and 0.155 87(2) nm, respectively, comparable with the standard bond length of $C_{(sp3)}$– $C_{(sp3)}$ [0.1541($\pm$3) nm] [22].

As shown in Fig. 2, one independent boric acid molecule in the asymmetic unit, together with its centrosymmetrically-related partner, was connected by a pair of O—H···O hydrogen bonds to form a plane cyclic dimer. The atoms of the two boric acid dimer were perfectly co-planar, as indicated by the torsion angle B(1)—O(1)···O(3A)—B(1A) = 0.6°. The outboard hydroxyl groups of the dimer joined carboxyl anions of EADA by a pair of O—H…O hydrogen bonds to

Table 2 Selected bond distances (nm) and bond angles (º)

$(n\text{-}C_4H_9)_4N^+C_{18}H_{13}O_4^- \cdot B(OH)_3$ (**1**)					
B(1)–O(2)	0.135 61(2)	C(9)–C(13)	0.151 39(2)	N(1)–C(19)	0.151 23(2)
B(1)–O(1)	0.135 83(2)	C(9)–C(15)	0.151 50(2)	C(19)–C(20)	0.151 45(2)
B(1)–O(3)	0.136 86(2)	C(9)–C(12)	0.155 38(2)	C(20)–C(21)	0.152 00(2)
O(4)–C(17)	0.133 88(2)	C(10)–C(11)	0.155 37(2)	C(21)–C(22)	0.151 96(2)
O(5)–C(17)	0.120 43(1)	C(11)–C(18)	0.151 99(2)	C(10)–C(14)	0.150 88(2)
O(6)–C(18)	0.127 75(1)	C(11)–C(12)	0.155 87(2)	C(10)–C(16)	0.151 52(2)
O(7)–C(18)	0.124 25(1)	C(12)–C(17)	0.151 07(2)		
O(2)–B(1)–O(1)	115.98(1)	C(17)–C(12)–C(11)	111.46(1)	N(1)–C(19)–C(20)	116.76(1)
O(2)–B(1)–O(3)	124.08(1)	C(9)–C(12)–C(11)	109.44(9)	C(19)–C(20)–C(21)	109.52(1)
O(1)–B(1)–O(3)	119.94(1)	C(1)–C(13)–C(9)	126.18(1)	C(22)–C(21)–C(20)	112.67(1)
C(13)–C(9)–C(15)	107.23(1)	C(5)–C(15)–C(9)	127.14(1)	C(14)–C(13)–C(9)	113.27(1)
C(13)–C(9)–C(12)	109.26(1)	C(16)–C(15)–C(9)	112.81(1)	C(4)–C(14)–C(10)	126.88(1)
C(18)–C(11)–C(12)	111.73(1)	C(8)–C(16)–C(15)	119.84(1)	C(13)–C(14)–C(10)	113.45(1)
C(10)–C(11)–C(12)	108.86(1)	C(15)–C(16)–C(10)	113.54(1)	O(5)–C(17)–O(4)	121.28(1)
C(17)–C(12)–C(9)	115.08(1)				
$(n\text{-}C_4H_9)_4N^+C_{18}H_{13}O_4^-$ (**2**)					
O(1)–C(17)	0.121 9(5)	C(29)–C(30)	0.151 4(4)	C(9)–C(12)	0.155 9(3)
O(2)–C(17)	0.130 2(5)	C(13)–C(9)	0.151 9(3)	C(12)–C(17)	0.144 8(5)
N(1)–C(27)	0.151 9(3)	C(14)–C(9A)	0.149 6(4)	C(12A)–C(9A)	0.155 9(2)
C(27)–C(28)	0.151 1(3)	C(4)–C(3)	0.138 0(4)	C(12)–C(12A)	0.151 9(5)
C(28)–C(29)	0.152 0(4)	C(9)–C(14A)	0.149 6(4)		
C(27)–N(1)–C(19)	111.29(14)	C(4)–C(14)–C(9A)	127.4(3)	C(17)–C(12)–C(9)	116.2(3)
C(28)–C(27)–N(1)	117.0(2)	C(13)–C(14)–C(9A)	113.4(2)	C(12A)–C(12)–C(9)	109.78(13)
C(27)–C(28)–C(29)	109.4(2)	C(14A)–C(9)–C(13)	107.6(2)	O(1)–C(17)–O(2)	123.8(4)
C(30)–C(29)–C(28)	112.7(3)	C(14A)–C(9)–C(12)	105.3(2)	O(1)–C(17)–C(12)	121.5(4)
C(1)–C(13)–C(9)	127.3(3)	C(13)–C(9)–C(12)	107.5(2)	O(2)–C(17)–C(12)	114.7(4)
C(14)–C(13)–C(9)	112.7(2)	C(17)–C(12)–C(12A)	118.8(3)		

Table 3 Hydrogen bond distances (nm), bond angles (º) and torsion angles (°) of tetramer of **1**

O(3)···O(6)	0.272 6	O(2)···O(7)	0.260 6	O(4)···O(6)	0.258 8
O(1)···O(3A)	0.273 2				
O(3)–H(7BA)···O(6)	179.5	O(2)–H(2BA)···O(7)	173.2	O(4)–H(4BA)···O(6)	171.2
O(1)–H(1BA)···O(3A)	173.5				
B(1)–O(3)…O(6)	113.6	B(1)–O(2)···O(7)	116.8	C(17)–O(4)···O(6)	104.4
B(1)–O(1)…O(3A)	118.2				
B(1)–O(2)…O(7)–C(18)	−14.6	C(18)–O(6)···O(3)–B(1)	19.5	C(17)–O(4)···O(6)–C(18)	−35.1
B(1)–O(1)…O(3A)–B(1A)	0.6				

Symmetry transformations: A: $-x$, $-y$, $-z$+1

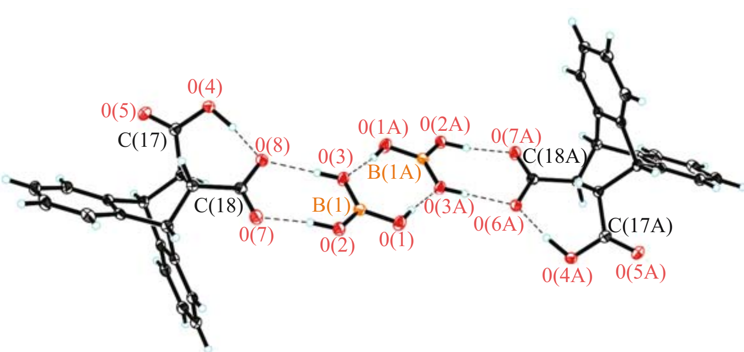

Fig. 2 The tetramer of EADA anions and boric molecules in compound **1**
Symmetry transformations: A: $-x$, $-y$, $-z+1$

form a tetramer (Fig. 2). The relationship between the carboxyl group and the boric acid molecule might be described by relevant torsion angles: B(1)—O(2)···O(7)—C(18) = −14.6°, and C(18)—O(6)···O(3)—B(1) = 19.5°. Tetramers were alternately arranged to generate a zigzag ribbon oriented parallel to the direction of the *b* axis. Rectangle unclosed channel host crystal lattices were formed by packing of the independent tetramers through the V-shape molecular skeleton of EADA. As shown in Fig. 3, the cross-sectional size of channels was about 2.30 nm × 0.93 nm, $(n\text{-}C_4H_9)_4N^+$ cations enclosed in these channels with regular geometry configuration were arranged in parallel forming two columns.

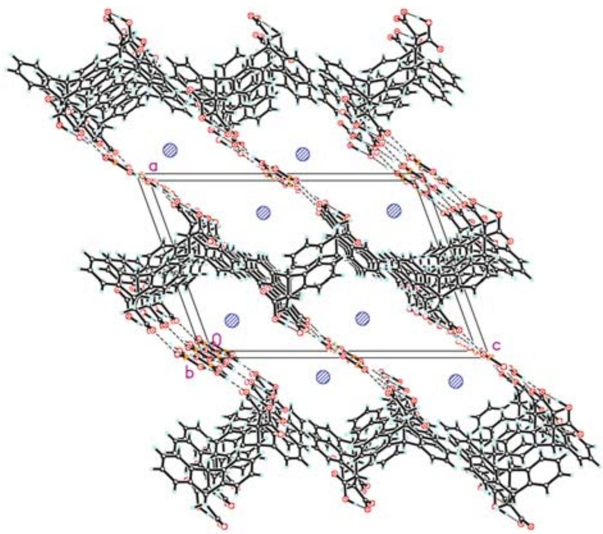

Fig. 3 Perspective view of 1 viewed along the *b* axis
Broken lines represent hydrogen bonds. $(n\text{-}C_4H_9)_4N^+$ are represented by large shaded spheres for clarity

3.2.2 Crystal structures of $(n\text{-}C_4H_9)_4N^+C_{18}H_{13}O_4^-$ (2)

The asymmetric unit of compound **2** consisted of a half $(n\text{-}C_4H_9)_4N^+$ cation and a half EADA anion. The EADA anion retained the two-fold symmetry and was located at the crystallographic 2-fold axis. A carboxyl group of EADA exhibited a two-fold orientation disorder, and the atoms of C(17), O(1), and O(2) were refined to site occupancies of 0.7 and 0.3, respectively. The atoms of phenyl rings of the host molecule also showed highly planar property, the dihedral angle between the two phenyl rings was 56.0°. As illustrated in Table 2, in compound **2**, the bond length of C(9)—C(12) of the bridged ethano, 0.155 9(3) nm, was slightly longer than the criterion bond length but in accord with relevant C—C bond length range (0.154 8(5) and 0.157 9(4) nm) [5,6]. It was noticed that the bond length of C(12)—C(12A) in compound **2** was slightly shorter than the criterion bond length of $C_{(sp3)}$—$C_{(sp3)}$ [0.1541(±3) nm] [22] (Fig. 4).

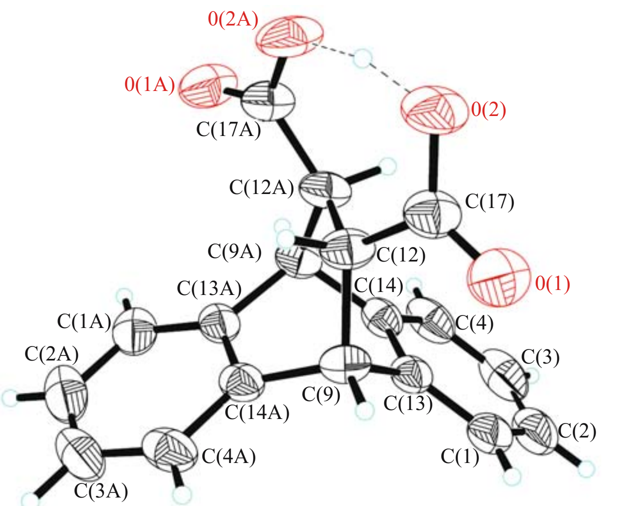

Fig. 4 ORTEP drawing of the EADA anion of $(n\text{-}C_4H_9)_4N^+\text{-}C_{18}H_{13}O_4^-$(**2**) with thermal ellipsoids shown at 30% probability
Symmetry transformations: A: $1-x, y, 1/2-z$

From Fig. 5, it could be seen that the host lattice was formed by EADA molecules through crystal lattice forces.

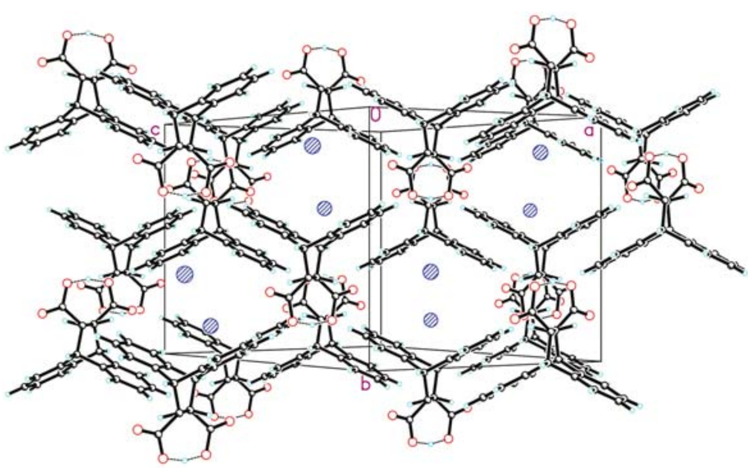

Fig. 5 Perspective view of the crystal structure of **2** showing channel system extending along the [101] direction
Well-ordered tetra-*n*-butylammonium cations represented by large spheres, were stacked in zigzag columns within each channel with cross-sectional size of about 1.10 nmx0.64 nm

Independent EADA anions were arranged in straight columns along the *a* axis to form a honeycomb-like host lattice with a big cross-section of about 1.10 nm × 0.64 nm, and the $(n\text{-}C_4H_9)_4N^+$ cations with regular geometric configuration were arranged in a zigzag column in the host lattice.

3.3 Structural features and relationships

In compound **1**, the dihedral angle between the two carboxyl plans of EADA was 35.5°. The EADA anions lost the two to fold symmetry with the relevant torsion angles being changed (C(12) − C(11) − C(18) − O(6) = 41.4° and C(11) − C(12) − C(17) − O(4) = 56.9°) due to forming hydrogen bond with boric acid molecules. The distance of O(4)…O(6) was 2.588 Å, indicating the existence of strong intrahost hydrogen bond. However, there was no hydrogen bond between EADA anions.

The structure of compound **1** could be compared with EADA-BuOH ($C_{18}H_{14}O_4 \cdot C_4H_{10}O$, **3**, monoclinic, $P\bar{1}$ space group, a = 1.197 98) nm, b = 1.023 3(9) nm, c = 0.897 4(6) nm, α = 84.79(4)°, β = 76.68(6)°, γ = 68.06(5)°, Z = 2) [6]. Although all of them were inclusion compounds containing two EADA anions and small solvent molecules with the same centro-symmetric hydrogen bonded tetramer in the host lattices, they had very different joint styles. Compound **1** was a stable host-guest inclusion with big rectangle-like cross-sectional channels containing two bulky $(n\text{-}C_4H_9)_4N^+$ cations due to the help of boric acid molecules. However, compound **3** was a adducts with small cavity in which no guest molecule was enclosed.

In compound **2**, EADA anions kept the two-fold symmetry, the dihedral angle between the two carboxyl plans was 24.2°, the distance of O(2)···O(2A) was 2.450 3 Å, shorter than that of **1**, and could be recognized as a relatively stronger intrahost hydrogen bond. The host crystal lattice of **2** was un-closed similar honeycomb-like one containing two bulky $(n\text{-}C_4H_9)_4N^+$ cations with regular geometry configuration. Therefore, compound **2** was a stable host-guest inclusion.

Although the title compounds were packed mainly through van der Waals interaction and hydrogen bonds, π-π stacking interaction also played an important role in the final network of the title compounds. The center distances of the two EADA anions' offset face-to-face benzene rings were about 0.405 9 nm in **1** and 0.454 nm in **2**, and the perpendicular distances of that were about 0.347 6 nm in **1** and 0.270 nm in **2**, indicating the existence of π–π stacking effect.

Based on this work, we can draw a conclusion that EADA is a good host molecule, which can form all kinds of host lattices by itself or with the help of small solvent molecules, producing stable inclusions containing bulky guest molecules.

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