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The role of secondary ammonium cations in controlling the conformation of C_3-symmetric acid moieties and its implication towards the design of supramolecular capsules

Tapas Kumar Adalder and Parthasarathi Dastidar*

Department of Organic Chemistry
Indian Association for the Cultivation Science (IACS)
2A and 2B Raja S. C. Mullick Road, Jadavpur, Kolkata, 700032, West Bengal (India)
Fax: (+91) 33-2473-2805
E-mail: ocpd@iacs.res.in; parthod123@rediffmail.com

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Abstract

This article reports an attempt to synthesise salt based supramolecular capsules derived from two C_3 symmetric tricarboxylic acids namely 2,4,6-trimethylbenzene-1,3,5-triacetic acid (**TMBTA**) and 2,4,6-triethylbenzene-1,3,5-triacetic acid (**TEBTA**) having flexible carboxymethyl arms. Both the acids displayed *syn-syn-anti* conformation of the carboxymethyl moiety as revealed from their single crystal structures. The concept of secondary ammonium dicarboxylate (SAD) synthon concept was attempted in order to bring all the carboxymethyl arms into *syn-syn-syn* conformation conducive for a capsular assembly. Reaction of various secondary amines with these two acids resulted in 16 salts, majority of them turned out to be 1 : 1 (acid : amine) salt as revealed from FT-IR data. The single crystal structures of 10 such salts revealed that the desired capsules were not formed. However, in most of the structures, the carboxylmethyl arms displayed *syn-syn-syn* conformation. Influence of the ammonium cations on the conformation of the flexible carboxymethyl arms of the acid moiety is discussed.

Introduction

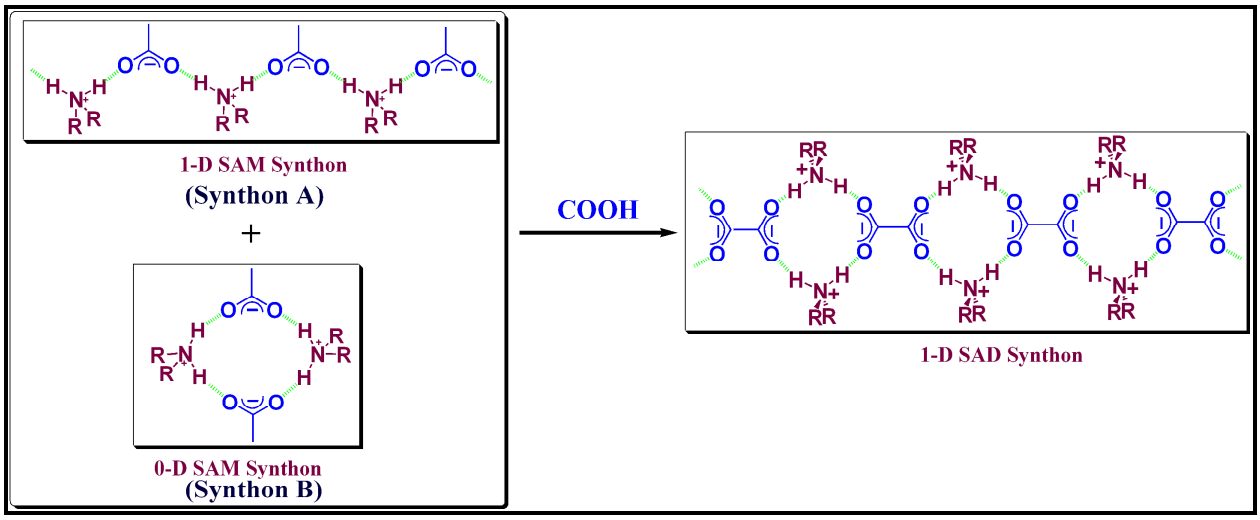
Supramolecular capsules[1] are an important class of self-assembled entity that can in principle separate a guest from the bulk solvent by entrapping it within the capsular assembly. There are quite a few reports towards this direction.[2] Metal assisted capsules have also been reported[3] wherein suitably designed ligands are brought together by exploiting metal-ligand coordination. Anion assisted capsular assemblies are also known.[4]

Organic salt formation, by far, is the easiest reaction to carry out. Mixing two components (acid and amine) at room temperature gives rise to almost near quantitative yield of the resulting salt. Charge assisted hydrogen bonding present in organic salt is strong and directional thereby making the material particularly suitable for real-life applications. Organic salt formation is found to be the method of choice for generating materials like non-linear optical materials (NLO),[5] aggregation induced emission (AIE) materials,[6] chiro-optical switches,[7] supramolecular plaster materials,[8] pharmaceutical salts[9] with improved bio-availability, low molecular mass gelators[10] etc. The only disadvantage, however, is the non-compatibility of the pKa of the reacting components.[11] Thus, quite often, the reacting components do not react in the desired molar ratio. Such limitation has nicely been exploited in pharmaceutical industry to produce pharmaceutical co-crystals[12] with improved pharmacological properties.

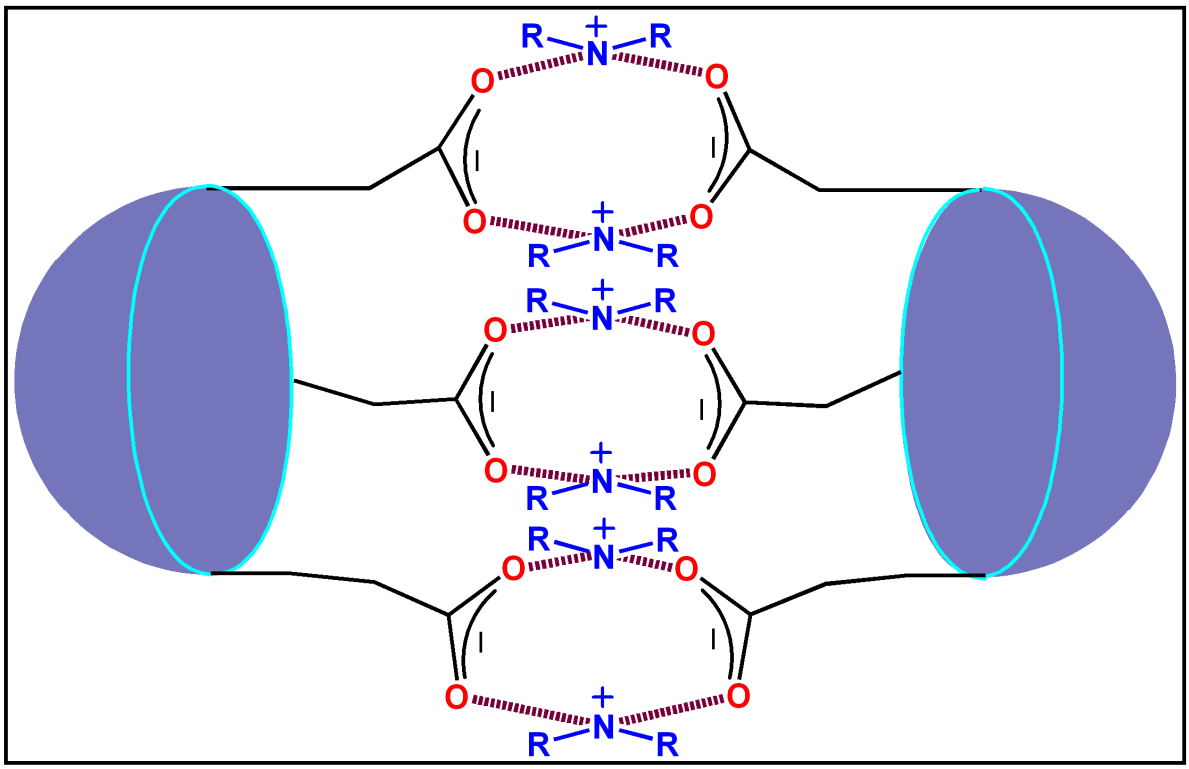
In this article, an attempt has been made to exploit organic salt based supramolecular synthon[13] to assemble suitably chosen half-capsule to a capsular assembly. For this purpose, we have decided to exploit secondary ammonium dicarboxylate (SAD) synthon.[14] Secondary ammonium monocarboxylate (SAM)[15] salts can give rise to two supramolecular synthons such as synthon A (a polymeric 1D network) and synthon B (a discrete 0D network). By choosing a dicarboxylic acid instead of a monocarboxylic acid, 1D hydrogen bonded network in such salts could be ascertained; in such network, synthon B could be seen. However, by virtue of the bis-functionality of the dicarboxylic acid, the overall network turned out to be a 1D polymeric chain (Scheme 1). It may be mentioned here that 1D synthons such as SAM and SAD have crucial role to play in supramolecular gelation.[14, 15] In order to create a capsular assembly, we thought it was worthwhile to exploit

SAD synthon to assemble two half-capsule into a capsular assembly (Scheme 2). Thus, we decided to work with two aromatic tripodal tricarboxylic acids namely **TMBTA** and **TEBTA**, respectively which can be considered as a half-capsule if the flexible carboxymethyl arms adopt *syn-syn-syn* conformation. If these tricarboxylic acids react with secondary amine in 1 : 3 (acid : amine) molar ratio in their *syn-syn-syn* conformation, the resultant assembly could be a supramolecular capsule sustained by the hydrogen bonded network resembling the SAD synthon. Thus, we reacted **TMBTA** and **TEBTA** with various secondary amines to form 16 salts (Scheme 3) of which 10 salts could be crystallized and their single crystal structures (Table 1) were determined. The role of the various cationic species and the subsituents (methyl/ethyl) on the aromatic ring on the conformation of the carboxymethyl moieties and their supramolecular architectures in these salts has been discussed.

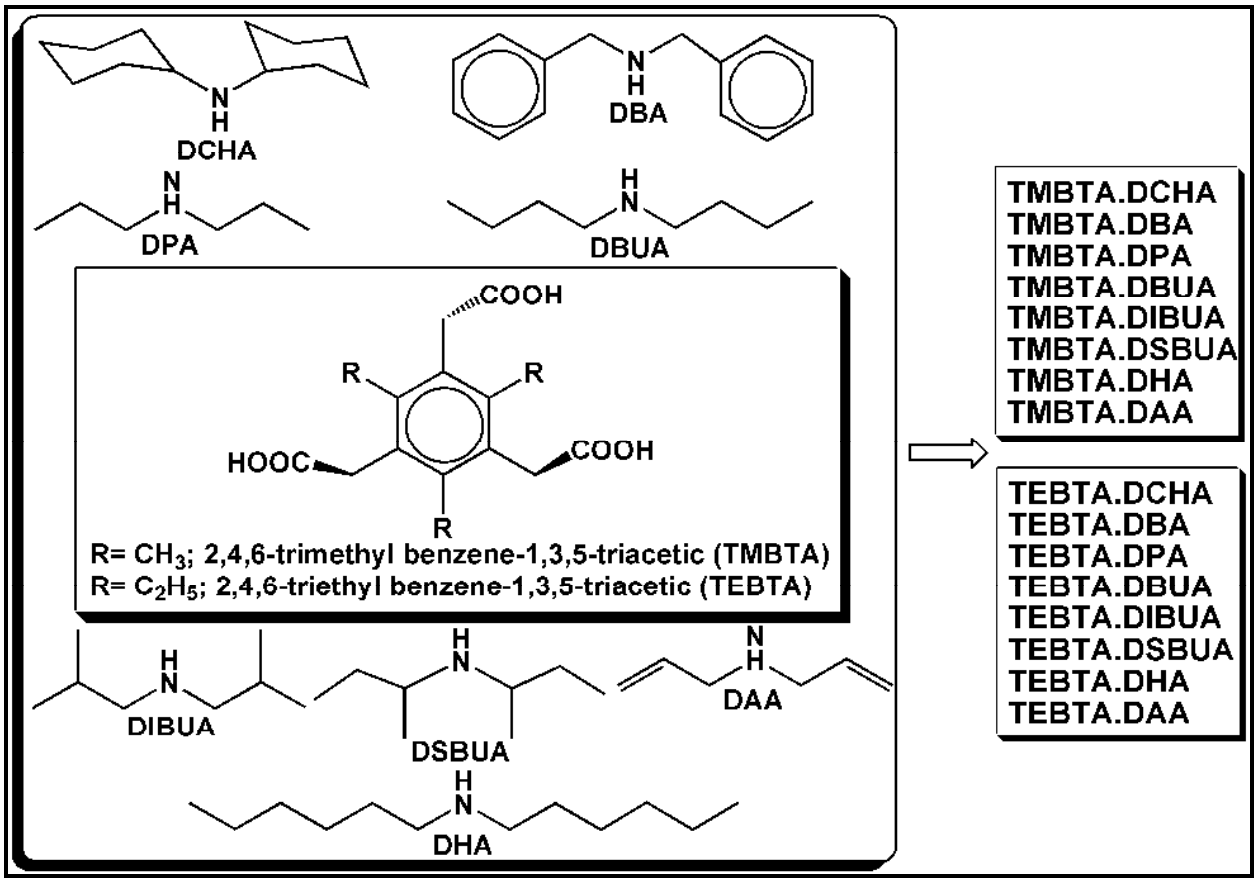
<<Table 1 is appended at the end of this document>>



Scheme 1. Transition of SAM synthon to 1D SAD synthon.



Scheme 2. Desired salt based supramolecular capsular assembly.



Scheme 3. Salts studied in this article.

Results and Discussion

Our best efforts resulted in crystallization of the parent acids namely **TMBTA** and **TEBTA** and 10 salts which were subjected to single crystal X-ray diffraction studies (Table 1).

Single crystal structures of the parent acids TMBTA and TEBTA.

The single crystal structure of the parent acids were isomorphous and displayed *syn-syn-anti* conformation for the carboxymethyl arms. Typical carboxylic acid dimer synthon was observed in both the acids resulting in a 2D hydrogen bonded sheet architecture. While lattice occluded EtOH molecules were present within the cavity of the 2D sheet of **TMBTA**, such occlusion of any solvent was not observed in ethyl analogue namely **TEBTA** presumably because of the steric bulk of the ethyl moiety significantly reducing the cavity size (Fig. 1 and ESI).

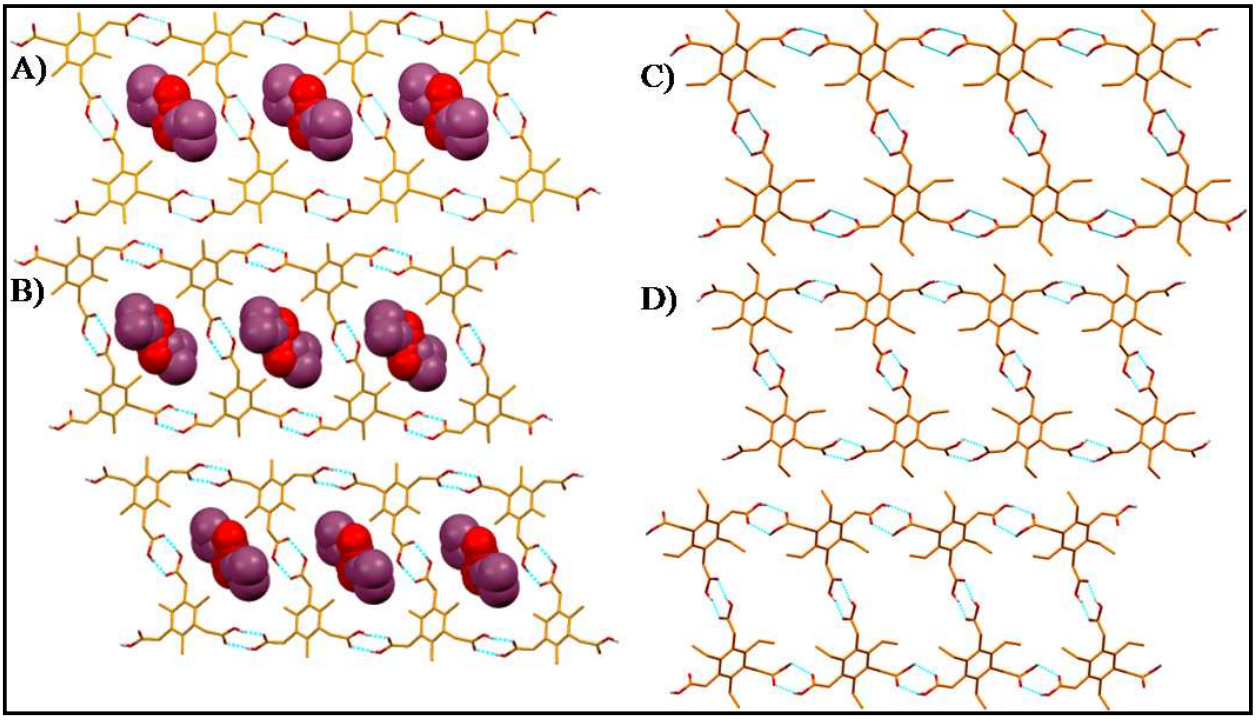


Fig.1. Crystal structure illustration, **TMBTA:** A) displaying 1-D hydrogen bonded tape with occluded disordered ethanol, B) parallel packing of the 1-D tapes; **TEBTA**: C) 1-D hydrogen bonded tapes, D) parallel packing of the 1-D tapes.

Single crystal X-ray diffraction.

Crystal structures of TMBTA.DCHA and TEBTA.DCHA. The FT-IR spectra of the bulk solid of these salts indicated the formation of 1: 3 (acid : amine) salts. However, crystal structure analyses revealed that **TMBTA.DCHA** was 1: 3 salt whereas the ethyl analogue i.e. **TEBTA.DCHA** was 1: 1 salt. The carboxymethyl group in both the cases displayed *syn-syn-anti* conformation. Both the salts displayed a 3D hydrogen bonded network containing lattice occluded hydrogen bonded water molecules. While the 1: 3 salt i.e. **TMBTA.DCHA** was mainly governed by ammonium-carboxylate hydrogen bonding interactions, the ethyl analogue being 1:1 salt displayed both ammonium-carboxylate and carboxylic acid-carboxylate interactions. Besides, the lattice occluded water molecules were held strongly via O-H•••O interactions involving carboxylate for **TMBTA.DCHA** and carboxylate and carboxylic acid for **TEBTA.DCHA** (Fig. 2 and ESI).

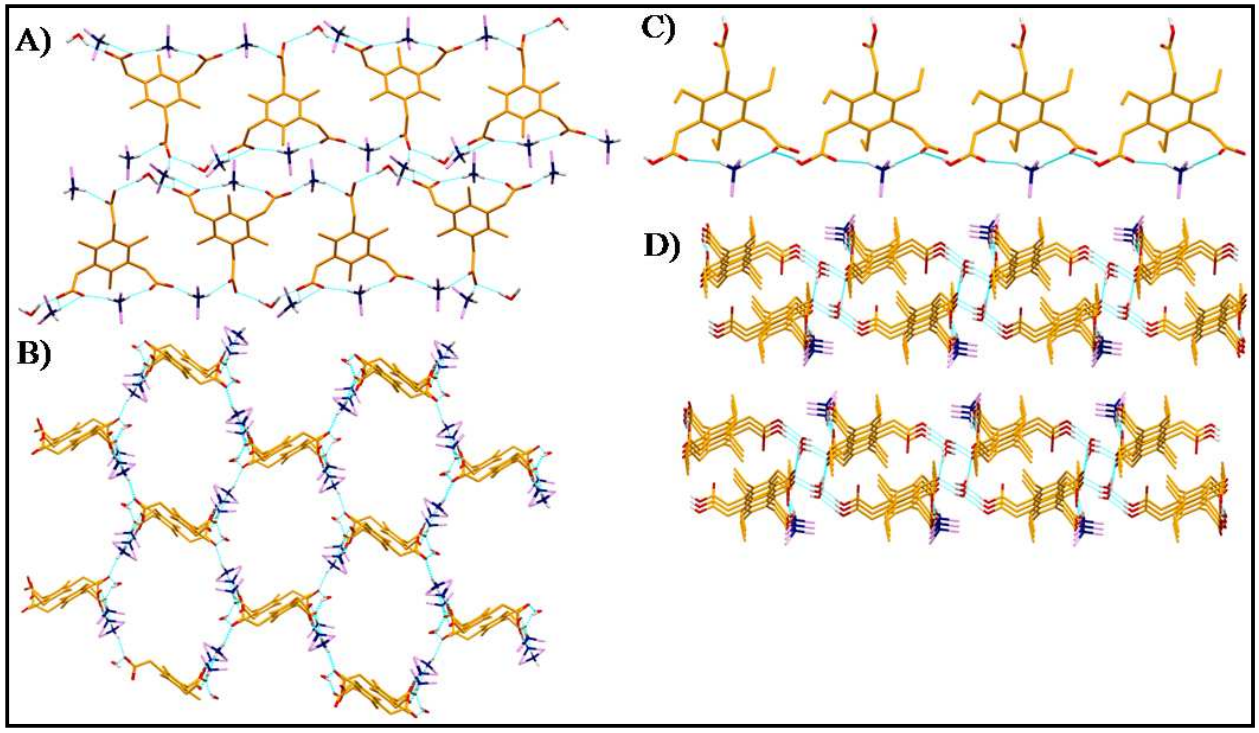


Fig.2. Crystal structure illustration, **TMBTA.DCHA**: A) assembly of the salt displaying various hydrogen bonding, B) 3D hydrogen bonded network. Carbon atoms of the ammonium cations were not shown for clarity; **TEBTA.DCHA**: C) 1D hydrogen bonded chain, D) parallel packing of the 2D hydrogen bonded layers.

Crystal structures of TMBTA.DPA and **TEBTA.DPA.** In these salts the desired stoichiometry of 1: 3 (acid : amine) was not observed in the bulk solids as revealed by the FT-IR data. The crystal structure analyses revealed that both the salts were 1: 1 (acid : amine). While the asymmetric unit of **TMBTA.DPA** contained one ion pair, the ethyl analogue (**TEBTA.DPA**) displayed the presence of four ion pair in the asymmetric unit. In both the cases, the carboxymethyl arms of the anionic moiety displayed *syn-syn-syn* conformation. The mono-anionic carboxylate moieties were held together by the carboxylic acid-carboxylate hydrogen bonding interactions resulting in a 2D sheet architecture in both the structures. Such 2D sheets were packed in parallel fashion and the ammonium cations were intercalated within the interstitial space of the 2D layers sustained by the ammonium-carboxylate interactions involving the ammonium cations and carboxylic moieties. While π-π interactions were observed in **TMBTA.DPA**, the ethyl analogue failed to show such interactions presumably because of the steric hindrance of the ethyl groups (Fig. 3 and ESI). Surprisingly, the salt pairs **TMBTA.DIBUA and TEBTA.DIBUA**, and **TMBTA.DAA** and **TEBTA.DAA** were found to be iso-structural with the salt pair **TMBTA.DPA and TEBTA.DPA** and therefore, the detailed structural features of these salts were not discussed herein (ESI).

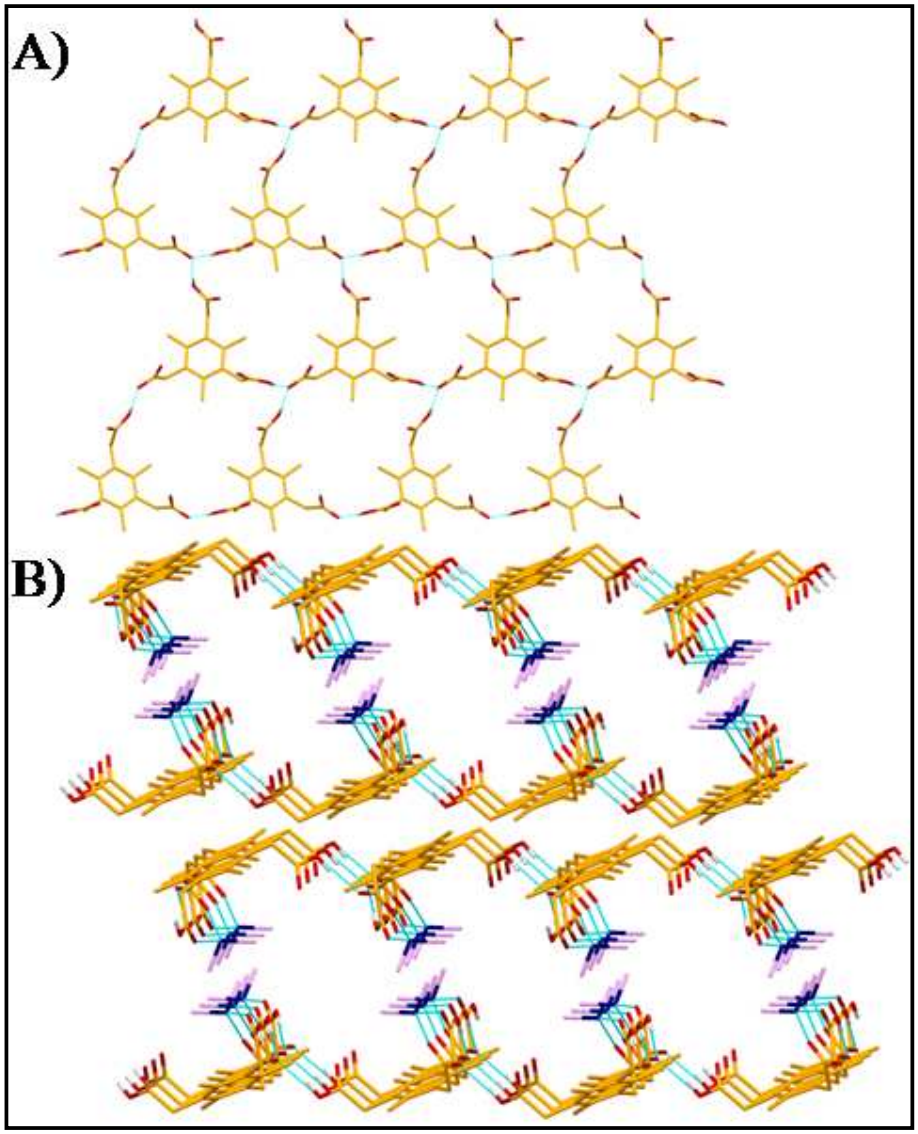


Fig.3. Crystal structure illustration of **TMBTA.DPA**; A) 2D hydrogen bonded network of the anionic moieties, B) parallel packing of 2D layer displaying intercalation of ammonium cation and π-π stacking. The disordered atoms as well as the alkyl chains of the cation were not shown for clarity. The crystal structure of the iso-structural salts namely **TEBTA.DPA. TMBTA.DIBUA, TEBTA.DIBUA**, **TMBTA.DAA** and **TEBTA.DAA** were not shown herein (see supporting information for details).

Crystal structures of TMBTA.DSBUA and TEBTA.DSBUA. The FT-IR data revealed that both the salts were not of the desired stoichiometry i.e. 1: 3 (acid: amine). The salts were 1:1 (acid: amine) as indicated by the single crystal structures. The mono-anionic acid moieties in both the salts displayed a 2D hydrogen bonded network sustained by the carboxylic acid-carboxylate hydrogen bond; the 2D network in **TMBTA.DSBUA** displayed corrugated sheet structure whereas that of in **TEBTA.DSBUA** was somewhat planar. In **TMBTA.DSBUA**, the cationic species were intercalated via the ammonium-carboxylate hydrogen bonding within the interstitial space generated due to parallel packing of the 2D sheet. On the other hand, the ammonium cations were located within the space between the bilayer packing of the 2D sheets in **TEBTA.DSBUA** sustained by the ammonium-carboxylate hydrogen bonding. Lattice occluded water molecules were also observed within the bilayer structure stabilized by the water-carboxylate hydrogen bonding interactions (Fig.4 and ESI).

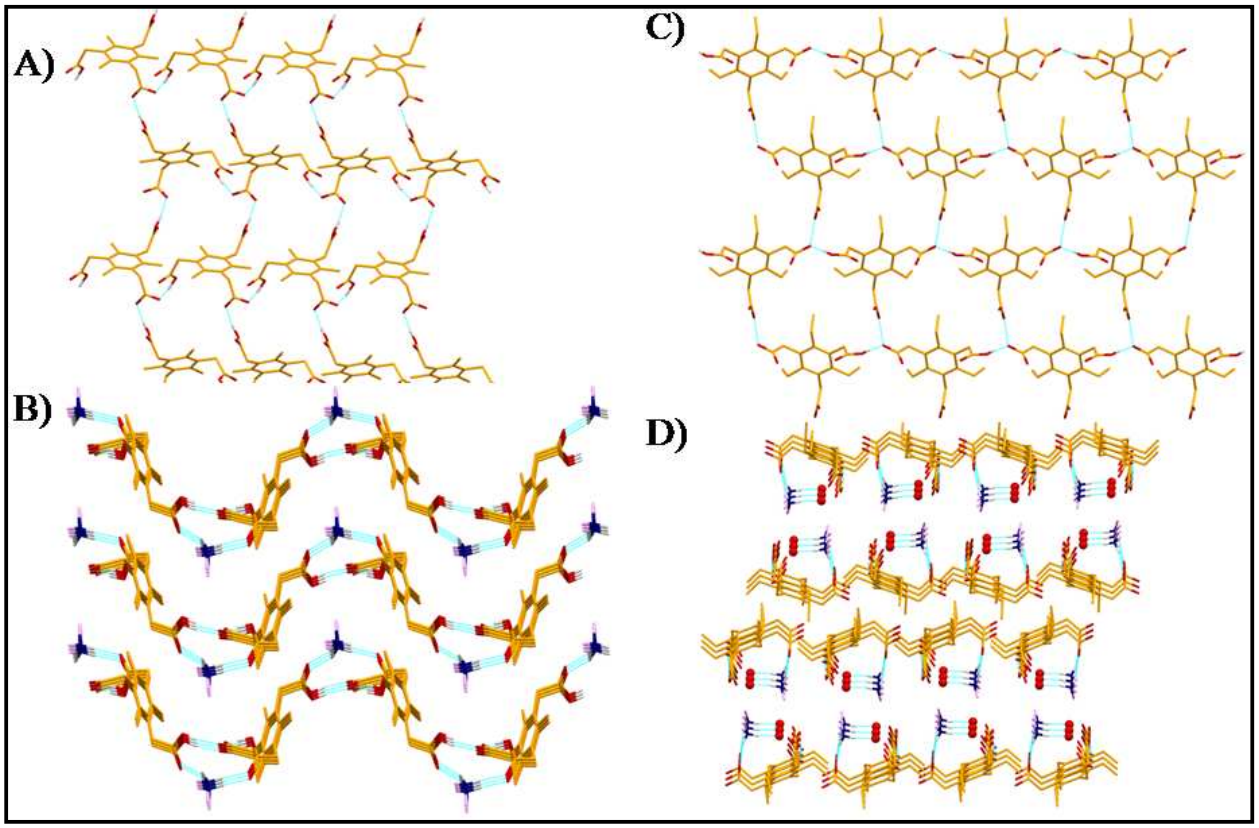


Fig.4. Crystal structure illustration, **TMBTA.DSBUA**: A) 2-D corrugated hydrogen bonded sheet structure of the anionic species; B) parallel packing of the corrugated sheets displayed intercalated cationic species sustained by hydrogen bonding; **TEBTA.DSBUA**: C) 2-D hydrogen bonded sheet of the anions; D) parallel packing of the 2D layered structures. Carbon atoms of the disordered **DSBUA** cations were not shown for clarity; red ball represents solvent water oxygen atom.

The pertinent features and parameters of the crystalline solids discussed above are given in Table 2. The foregoing discussions on the crystal structures of the parent acids and their 10 different salts pointed out to the following important features. The parent acid (**TMBTA**) containing methyl substituents on the aromatic ring did not display the desired *syn-syn-syn* conformation of the carboxymethyl arms supposedly required for a capsule formation. The steric bulk introduced by the ethyl substituent in the parent acid **TEBTA** also proved to be unsuccessful in orienting all the carboxymethyl arms to *syn-syn-syn* conformation. Typical carboxylic acid dimer synthon was observed in both the parent acids that resulted in a 2D hydrogen bonded sheet architecture. The FT-IR data of the bulk solid revealed that reactive components of the salts did not react in the desired 1: 3 (acid : amine) molar ratio in most of the cases (except **TMBTA.DCHA** and **TEBTA.DCHA**) presumably because of the pKa incompatibility. However, except **TMBTA.DCHA**, all the other salts turned out to be 1: 1 (acid : amine) as revealed by the crystal structures. Therefore, none of the salts displayed capsule formation. Majority of the salts (7 salts), however, displayed *syn-syn-syn* conformation for the carboxylmethyl arms thereby indicating that the methyl or ethyl substituents on the aromatic ring apparently did not have much influence on the resulting conformation of the acid moiety. However, the cationic moiety seemed to have a profound effect on the resultant acid conformation as well as the supramolecular architectures. The cation having alicyclic substituent (e.g. **TMBTA.DCHA and TEBTA.DCHA**) resulted in *syn-syn-anti* conformation for the acid moiety and 1D arrangement in the primary supramolecular architecture of the ion pairs. On the other hand, the rest of the salts derived from cations having acyclic substituents were isostructural displaying mostly *syn-syn-syn* conformation of the acid moieties and a 2D hydrogen bonded sheet architecture involving the anions that ultimately generated bilayer structures except in the case of **TMBTA.DSBUA**; in this case, *syn-syn-anti* conformation of the carboxymethyl arms and intercalation of the cations within the interstitial space generated by the parallel packing of the 2D corrugated sheet comprised of the anionic moieties were observed.

<<Table 2 is appended at the end of this document>>

Powder X-ray diffraction (PXRD). PXRD data were recorded for all the samples including free acids for which the single crystal structures were determined. While the experimental PXRD pattern of the free acid **TMBTA** was in excellent agreement with the simulated PXRD pattern generated from SXRD data. Most of the PXRD patterns of the salts displayed significant disagreement; the reason for severe disagreement in PXRD patterns for the salts **TMBTA.DCHA**, **TEBTA.DCHA** and **TEBTA.DSBUA** could be attributed to the desolvation of the occluded solvent molecules during PXRD data collection. For the rest, presence of more than one crystalline phase in the bulk solid must be contributing towards such disagreement (Fig.5).

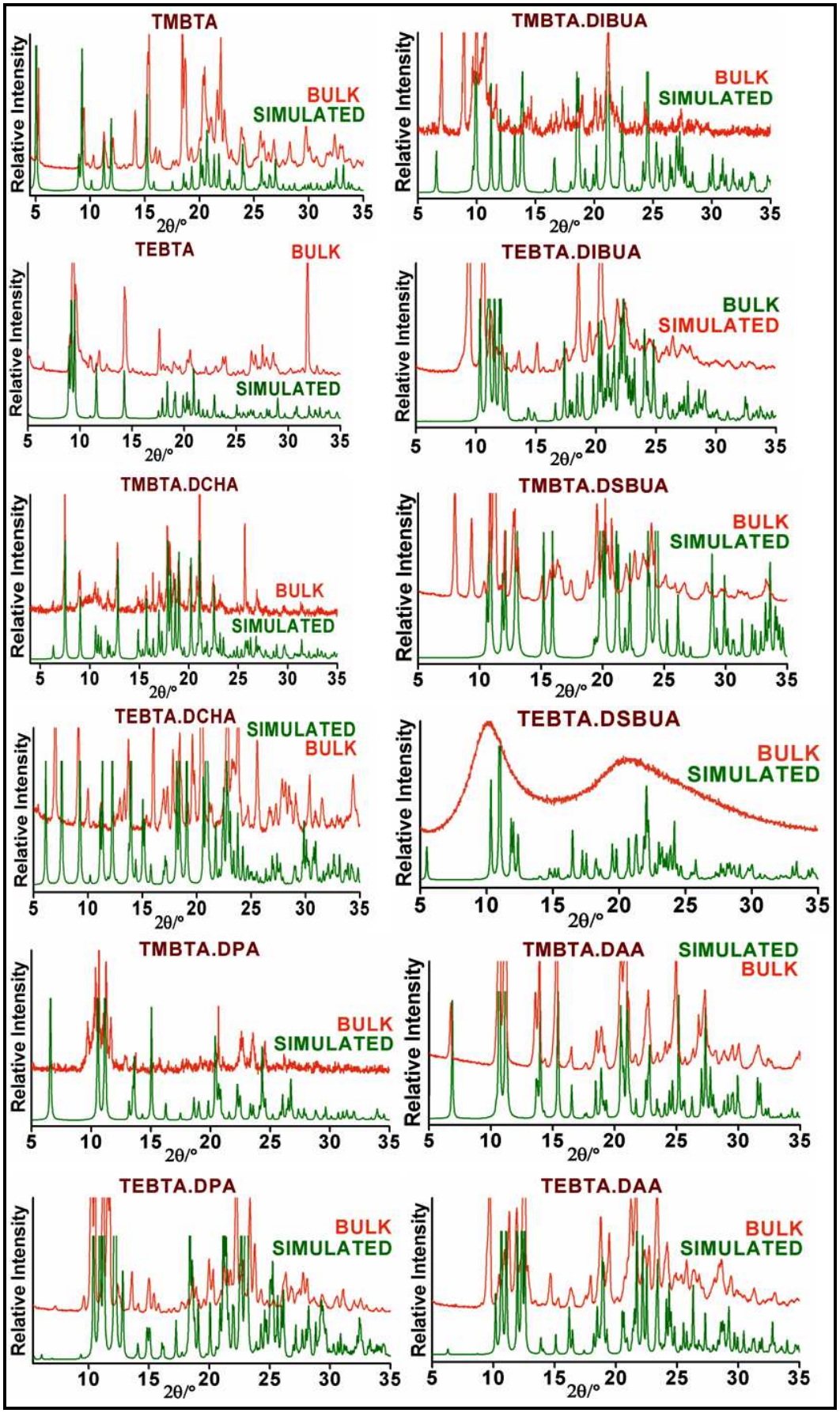


Fig.5. PXRD of the free acids and the salts under various conditions.

Conclusions

An attempt has been made to assemble C_3-symmetric triacids having flexible carboxymethyl arms into supramolecular capsules by invoking supramolecular synthon concept. However, the reactions of the corresponding acids and the amines did not take place in the desired 1 : 3 (acid : amine) molar ratio and as a result, none of them displayed capsule formation. Majority of the single crystal structures of the salts displayed *syn-syn-syn* conformation for the carboxymethyl arms which is one of the most crucial requirements for such a capsular self-assembly. While cationic the moiety having alicyclic substituents lead to the formation of *syn-syn-anti* conformation of the acid moiety, the acylic substituents on the cationic moiety seemed to have influenced the formation of *syn-syn-syn* conformation. Although we have not achieved the desired supramolecular capsule, the overall results indicate the conformation of the acid moiety could be controlled to the desired *syn-syn-syn* conformation by choosing appropriate cationic species.

Experimental Section

Materials and Methods. The various secondary amines, all other chemicals required to synthesize the parent acid[16, 17, 18] molecules were commercially available and used as such without further purification. Solvents were of L. R. grade and used without further distillation. Melting point was determined by Veego programmable melting point apparatus, India. IR spectra were recorded on a FT-IR instrument (FTIR-8300, Shimadzu). ^{1}H NMR spectra were recorded on a Brukar AVANCE DPX 300 (for 300MHz) and III 500 (for 500 MHz).

Single crystal X-ray diffraction. Data were collected using MoKα (λ = 0.7107 Å) radiation on a BRUKER APEX II diffractometer equipped with CCD area detector. Data collection, data reduction, structure solution/refinement were carried out using the software package of SMART APEX. All structures were solved by direct method and refined in a routine manner. In most of the cases, non- hydrogen atoms were treated anisotropically. The most of the hydrogen atoms were fixed geometrically. The cationic part of the structures of the salts **TMBTA.DPA, TEBTA.DIBUA, TMBTA.DAA TEBTA.DAA** and **TEBTA.DSBUA** were found to be disordered; the C atoms of the alkyl moiety of the cations were disordered over two positions and they were refined using second variable of FVAR, PART and DFIX instructions of software package of SMART APEX. The resulting refinements were unable to resolve the various anomalous bond distances in the cationic moieties. However, the overall packings were established. In most of the cases, the crystals were of poor quality leading to the various alerts in the CIF Check report. The situation could not be improved by collecting fresh data on several crystals even at low temperature in some cases. Appropriate author responses have been incorporated in the CIF. CCDC (CCDC No. 929277-929288) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Powder X-ray diffraction. Powder diffraction data for the bulk solid were recorded by placing the well grounded solid on a PXRD machine (BRUKER AXS D8 Advance) at a scan speed of 0.5º/min.

†Electronic Supplementary Information (ESI) available: (FT-IR, ^{1}H NMR, detailed crystal structure description and and molecular plot with hydrogen bonding parameters). See DOI: 10.1039/b000000x/

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Table 1. Crystallographic parameters

Crystal parameters	TMBTA	TEBTA	TMBTA.DCHA	TEBTA.DCHA	TMBTA.DPA	TEBTA.DPA	TMBTA.DIBUA	TEBTA.DIBUA	TMBTA.DAA	TEBTA.DAA	TMBTA.DSBUA	TEBTA.DSBUA
CCDC No	929277	929278	929288	929282	929286	929279	929287	929283	929281	929284	929285	929280
Moiety formula	$2(C_{15}H_{18}O_6).C_2H_6O$	$C_{18}H_{24}O_6$	$3(C_{12}H_{24}N^+).C_{15}H_{15}O_6^{3-}.H_2O$	$C_{12}H_{24}N^+.C_{18}H_{23}O_6^-.H_2O$	$C_6H_{16}N^+.C_{15}H_{17}O_6^-$	$C_6H_{16}N^+.C_{18}H_{23}O_6^-$	$C_8H_{20}N^+.C_{15}H_{17}O_6^-$	$C_8H_{20}N^+.C_{18}H_{23}O_6^-$	$C_6H_{12}N^+.C_{15}H_{17}O_6^-$	$C_6H_{12}N^+.C_{18}H_{23}O_6^-$	$C_8H_{20}N^+.C_{15}H_{17}O_6^-$	$C_8H_{20}N^+.C_{18}H_{23}O_6^-.H_2O$
Formula weight	634.67	336.37	856.25	535.70	379.36	437.56	423.54	461.58	391.46	433.54	423.54	967.28
Crystal size/mm	0.30x0.27x0.24	0.28x0.25x0.20	0.36x0.28x0.20	0.60x0.40x0.23	0.31x0.27x0.20	0.37x0.14x0.11	0.40x0.35x0.32	0.40x0.37x0.33	0.35x0.23x0.22	0.41x0.38x0.34	0.60x0.55x0.49	0.35x0.32x0.28
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	P 2_1/n	P 2_1/n	Fdd2	P 2_1/n	P 2_1/c	P 2_1/c	P 2_1/c	P 2_1/c	P 2_1/c	P $ca2_1$	P 2_1	P 2_1/c
a /Å	10.1249(7)	10.125(6)	29.446(14)	17.7425(9)	14.566(10)	30.0728(8)	14.494(5)	31.663(3)	13.957(4)	16.681(2)	8.405(11)	33.1689(10)
b/Å	4.7655(3)	4.993(3)	39.144(19)	8.7392(5)	9.991(7)	9.9777(3)	8.794(5)	10.0805(10)	10.086(3)	10.1817(14)	16.69(2)	10.1077(3)
c /Å	35.020(3)	37.33(2)	17.410(8)	19.5395(10)	17.129(11)	16.8414(4)	19.179(5)	16.7716(17)	17.006(5)	28.164(4)	9.156(13)	16.6962(5)
$\alpha/^0$	90	90	90	90	90	90	90	90	90	90	90	90
$\beta/^0$	93.387(2)	93.079(15)	90	102.293(2)	112.740(13)	105.730(2)	111.665(5)	104.662(2)	113.026(5)	90	117.32(8)	103.568(2)
$\gamma/^0$	90	90	90	90	90	90	90	90	90	90	90	90
Volume/$Å^3$	1686.8(2)	1884(2)	20067(16)	2960.2(3)	2299(3)	4864.1(2)	2271.9(16)	5178.8(9)	2203.1(11)	4783.5(11)	1141(3)	5441.4(3)
Z	2	4	16	4	4	4	4	8	4	8	2	4
F(000)	664	720	7552	1168	792	1904	920	2000	808	1848	460	2024
μ MoKα /mm^{-1}	0.096	0.089	0.074	0.084	0.081	0.085	0.088	0.083	0.085	0.085	0.088	0.083
Temperature/K	293(2)	293(2)	100(2)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)
R_{int}	0.0465	0.0640	0.0507	0.0383	0.0473	0.1044	0.0367	0.0596	0.0456	0.0504	0.1200	0.0739
Range of h, k, l	-11/11, -5/5, -40/39	-8/8, -4/4, -31/31	-34/34, -46/42, -20/20	-23/23, -11/11, -25/25	-17/16, -11/11, -15/20	-35/35, -11/11, -19/19	-17/17, -10/10, -23/23	-30/30, -9/9, -16/16	-16/16, -11/11, -20/20	-15/15, -9/9, -26/26	-9/9, -19/19, -10/10	-33/33, -10/10, -16/17
θmin/max/°	1.16/2 4.03	1.09/17.50	6.22/25.00	1.41/27.50	2.41/25.00	0.70/24.96	2.58/25.50	0.66/20.18	1.59/25.00	1.45/ 19.47	2.44/24.99	0.63/21.29
Reflections collected/unique/ observed [I>2σ(I)]	13712/ 2655/1988	7322/1192/917	43331/4494/3779	50741/6795/5693	10415/4035/2223	71057/8471/5544	24321/4245/3380	30072/4950/3719	11542/2642/2186	29880/4133/3822	10904/4018/3686	62465/6060/5007
Data/restraints/ parameters	2655 /0/ 217	1192/0/224	4494/1/561	6795/0/356	4035/0/254	8471/1/574	4245/0/280	4950/2/613	2642/1/255	4133/4/567	4018/1/286	6060/2/634
Goodness of fit on F^2	1.081	1.161	1.147	1.017	1.016	1.085	1.066	1.079	1.067	0.993	1.047	1.007
Final R indices [I>2σ(I)]	R_1 = 0.0858 wR_2 = 0.2555	R_1 = 0.0792 wR_2 = 0.2436	R_1 = 0.0390 wR_2 = 0.0987	R_1 = 0.0411 wR_2 = 0.1168	R_1 = 0.0866 wR_2 = 0.2308	R_1 = 0.1053 wR_2 = 0.2468	R_1 = 0.0502 wR_2 = 0.1366	R_1 = 0.0495 wR_2 = 0.1327	R_1 = 0.0617 wR_2 = 0.1932	R_1 = 0.0368 wR_2 = 0.0998	R_1 = 0.0630 wR_2 = 0.1606	R_1 = 0.0767 wR_2 = 0.2162
R indices (all data)	R_1 = 0.1049 wR_2 = 0.2743	R_1 = 0.0938 wR_2 = 0.2647	R_1 = 0.0502 wR_2 = 0.1067	R_1 = 0.0508 wR_2 = 0.1297	R_1 = 0.1429 wR_2 = 0.2754	R_1 = 0.1579 wR_2 = 0.2727	R_1 = 0.0628 wR_2 = 0.1483	R_1 = 0.0686 wR_2 = 0.1474	R_1 = 0.0717 wR_2 = 0.2040	R_1 = 0.0405 wR_2 = 0.1031	R_1 = 0.0673 wR_2 = 0.1643	R_1 = 0.0903 wR_2 = 0.2351

Table 2: The pertinent features and parameters of the parent acids and their salts.

Structural information	**TMBTA**	**TEBTA**	**TMBTA.DCHA**	**TEBTA.DCHA**	**TMBTA.DPA**	**TEBTA.DPA**	**TMBTA.DIBUA**	**TEBTA.DIBUA**	**TMBTA.DAA**	**TEBTA.DAA**	**TMBTA.DSBUA**	**TEBTA.DSBUA**
ν_{COOH}/ν_{COO-} (cm^{-1})	1697	1699	1610	1564	1701 and 1585	1703 and 1562	1708 and 1552	1695 and 1566	1732 and 1556	1716 and 1570	1716 and 1626	1716 and 1566
Asymmetric unit/moiety	1 acid and 1/2 ethanol	1 acid	3 cations, 1anion and 1 H_2O	1 cation, 1anion and 1 H_2O	1 cation and 1anion	2cations and 2 anions	1 cation and 1anion	2 cations and 2 anions	1 cation and 1anion	2 cations and 2anions	1 cation and 1anion	2 cations and 2 anions
C-O distances/Å	1.205(5)-1.208(5) 1.299(5)-1.314(5)	1.192(10)-1.211(9) 1.309(9)-1.317(10)	1.241(3)-1.255(2)	1.2393(14)-1.2682(15) 1.1914(17)-1.3165(14)	1.218(4)-1.281(4) 1.209(5)-1.308(4)	1.226(6)-1.281(6) 1.202(6)-1.314(6)	1.203(3)-1.314(2) 1.234(2)-1.272(2)	1.195(4)-1.312(4) 1.220(4)- 1.277(4)	1.209(4)-1.326(3) 1.223(4)-1.287(3)	1.204(5)-1.331(5) 1.215(6) -1.294(5)	1.205(4)-1.289(4) 1.236(4)-1.284(4)	1.209(5)-1.318(6) 1.189(6)- 283(6)
Salt stoichiometry (acid : amine)	-	-	1 :3	1 : 1	1 : 1	1 : 1	1 : 1	1 : 1	1 : 1	1 : 1	1 : 1	1 : 1
Conformation of the Carboxymethyl arm	*syn-syn-anti*	*syn-syn-anti*	*syn-syn-anti*	*syn-syn-anti*	*syn-syn-syn*	*syn-syn-syn*	*syn-syn-syn*	*syn-syn-syn*	*syn-syn-syn*	*syn-syn-syn*	*syn-syn-anti*	*syn-syn-syn*
Torsional angles involving carboxymethyl arms and the phenyl ring	93.2, 98.1 and 100.8	92.8, 97.8 and 108.7	92.2, 92.4 and 94.5	94.4, 97.7 and 98.0	92.2, 92.4 and 92.8	-90.00- 90.56, -92.95- - 95.77-and -93.48-92.75	94.0, 97.9 and 98.5	90.9-91.7, 94.5-94.7 and 95.2-97.1	91.2, 92.0 and 95.7	91.6-92.0, 92.4-93.2 and 94.9-96.7	92.4, 94.6 and 102.2	89.9-90.5, 89.8-90.4 and 93.9-94.5
O-H•••O/Å	2.661(5)-2.698(4)	2.649(9)-2.679(8)	-	2.5572(12)	2.553(4)-2.639(5)	2.520(5)- 2.582(5)	2.575(2) -2.578(2)	2.545(3)-2.637(3)	2.539(3)-2.622(3)	2.478(4)-2.620(4)	3.187(4)-2.429(4)	2.555(5)-2.573(4)
∠O-H•••O/°	168.8-176.2	121.2-165.6	-	163.6	168.8-174.2	164.8°-173.2	161.2-164.9	168.5-174.5	172.8-173.6	165.5-174.5	120(4)-159(5)	171.6-173.7
N-H•••O/Å	-	-	2.674(3)-3.107(3)	2.7630(13)-2.8101(13)	2.771-2.848	2.765(7)-2.798(7)	2.803(2)-2.872(3)	2.769(4)-2.796(4)	2.735(4)-2.815(3)	2.711(5)-3.076(5)	2.784(4)-2.792(4)	2.845(7)-2.885(6)
∠N-H•••O/°	-	-	130.8-172.3	156.6-164.2	-	152.8-165.3	152.6-171.2	150.2-172.2	166.9-179.4	120.0-174.2	154.5-171.2	163-167
π-π Interaction/Å	-	-	-	-	4.04	-	3.96	-	4.0	-	-	-

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Table of contents. Single crystal structures of a series organic salt derived from C_3-symmetric tricarboxylic acids having flexible carboxymethyl arms and secondary amines revealed that acyclic substituents of the secondary amine seemed to have profound influence in controlling the conformation of the carboxymethyl arms.