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

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Physico-chemical Data for the parent acid and salts

TMBTA: m.p. 253 °C; FT-IR (KBr pellet, cm^{-1}): 3091, 3014, 2951, 2845, 2727, 2627, 2549, 1697, 1415, 1321, 1298, 1228, 1170, 1022, 912, 827, 756, 682; ^{1}H NMR (500MHz, CD_3OD): δ (ppm) = 3.75 (s, 6H), 2.72 (q, J = 5.0 Hz, 6H).

TEBTA: m.p. 265 °C; (KBr pellet, cm^{-1}): 3097, 2991, 2970, 2929, 2879, 2864, 2729, 2626, 2544, 1699, 1653, 1456, 1417, 1319, 1226, 1174, 1039, 933, 904, 686; ^{1}H NMR (500MHz, CD_3OD): δ (ppm) = 3.75 (s, 6H), 2.73-2.68 (q, J = 7.5 Hz, 6H), 1.14-1.11 (t, J = 8.0 Hz, 9H).

TMBTA.DCHA: m.p. 148 °C; FT-IR (KBr pellet, cm^{-1}): 3458, 3427, 3417, 2937, 2854, 2810, 2756, 2756, 2725, 2696, 2667, 2929, 2598, 2551, 2519, 2459, 2420, 1610, 1568, 1556, 1452, 1371, 1352, 1315, 1259, 1249, 1055, 1033, 900, 813, 671, 594, 549, 488, 478; ^{1}H NMR (500MHz, CD_3OD): δ (ppm) = 3.63 (s, 6H), 3.02-2.97 (m, 6H), 2.24 (S, 9H), 1.93-1.65 (broad m, 30H), 1.33-1.11 (m, 36H).

TEBTA.DCHA: m.p. 152 °C; FT-IR (KBr pellet, cm^{-1}): 3400, 3157, 2931, 2856, 2796, 2752, 2725, 2700, 2663, 2632, 2607, 2526, 2501, 2428, 2360, 2169, 2061, 1944, 1564, 1487, 1452, 1444, 1367, 1313, 1267, 1247, 1057, 678, 653, 605, 588, 559, 547, 480, 445; ^{1}H NMR (300MHz, CD_3OD): δ (ppm) = 3.63 (s, 6H), 3.08-3.01(m, 6H), 2.72-2.64 (q, J = 7.0 Hz, 6H), 2.24 (S, 9H), 1.96-1.65 (broad m, 24H), 1.33-1.11 (m, 36H), 1.15-1.10 (t, J = 7.2 Hz, 9H).

TMBTA.DBA: m.p. 135 °C; FT-IR (KBr pellet, cm^{-1}): 3641, 3265, 3061, 3034, 2972, 2949, 2814, 2760, 2609, 2586, 2449, 1952, 1890, 1815, 1726, 1627, 1587, 1548, 1496, 1454, 1369, 1311, 1273, 1236, 1213, 1192, 1166, 1116, 1078, 1049, 1026, 1020, 1003, 972, 910, 887, 869, 831, 808, 749, 744, 696, 663, 601, 592, 570, 484; ^{1}H NMR (500MHz, CD_3OD): δ (ppm) = 7.38-7.35 (p, 17.0 Hz, 20H), 3.82 (s, 8H), 3.56 (s, 6H), 2.03 (s, 9H).

TEBTA.DBA: m.p. 142 °C; FT-IR (KBr pellet, cm^{-1}): 3410, 3400, 3111, 3088, 3063, 3034, 2964, 2928, 2872, 2843, 2791, 2764, 2739, 2658, 2598, 2476, 2457, 2424, 2386, 2351, 2339, 2177, 1620, 1564, 1496, 1483, 1456, 1431, 1377, 1313, 1271, 1249, 1211, 1193, 1165, 1070, 1043, 935, 918, 746, 734, 702, 677, 619, 588, 574, 536, 486, 466; ^{1}H NMR (500MHz, CD_3OD): δ (ppm) = 7.41-7.30 (m, 17.0 Hz, 10H), 3.82 (s, 8H), 3.80 (s, 4H), 3.65 (s, 6H), 2.49-2.46 (q, J = 8.0 Hz, 6H), 1.08-1.03 (t, J = 16.5 Hz, 9H).

TMBTA.DPA: m.p. 239 °C; FT-IR (KBr pellet, cm^{-1}): 3441, 3387, 3277, 3028, 2968, 2939, 2879, 2860, 2549, 2528, 2447, 2416, 2362, 2343, 1950, 1710, 1618, 1618, 1585, 1560, 1498, 1471, 1458, 1435, 1379, 1356, 1344, 1327, 1301, 1265, 1236, 1209, 1192, 1095, 1076, 1049, 1020, 956, 893, 860, 825, 798, 756, 686, 667, 623; ^{1}H NMR (500MHz, CD_3OD): δ (ppm) = 3.70 (s, 6H), 2. 65-2.62 (t, J = 8.0 Hz, 4H), 2.25 (s, 9H), 1.56-1.50 (p, J = 7.5 Hz, 4H), 0.92-0.89 (t, J = 7.0 Hz, 6H).

TEBTA.DPA: m.p. 242 °C; FT-IR (KBr pellet, cm^{-1}): 3410, 3028, 2966, 2935, 2877, 2551, 2449, 1703, 1680, 1614, 1562, 1556, 1489, 1454, 1433, 1369, 1329, 1269, 1228, 1201, 1089, 1068, 1049, 968, 933, 900, 839, 810, 788, 756, 698, 669, 621, 588; ^{1}H NMR (500MHz, CD$_3$OD): δ (ppm) = 3.68 (s, 6H), 2.73-2.63 (m, 10H), 1.60-1.52 (m, 4H), 1.15-1.29 (t, J = 7.5Hz, 9H), 0.94-0.91 (t, J = 7.5Hz, 6H).

TMBTA.DBUA: m.p. 243 °C, FT-IR (KBr pellet, cm^{-1}): 3479, 3444, 3417, 3263, 2960, 2933, 2874, 2814, 2791, 2779, 2575, 2486, 2428, 1633, 1614, 1556, 1469, 1373, 1261, 1184, 1147, 1107, 1076, 1060, 1045, 1020, 993, 949, 912, 873, 827, 796, 763, 738, 678, 669, 605, 565, 540, 474; ^{1}H NMR (500MHz, CD$_3$OD): δ (ppm) = 3.64 (s, 6H), 2. 69-2.66 (t, J = 8.0 Hz, 8H), 2.23 (s, 9H), 1.52-1.46 (p, J = 7.5 Hz, 8H), 1.35-1.1.28 (p, J = 7.5 Hz, 8H), 0.94-0.91 (t, J = 7.5 Hz, 12H).

TEBTA.DBUA: m.p. 249 °C; FT-IR (KBr pellet, cm^{-1}): 3520, 3500, 3429, 3417, 3279, 3227, 2962, 2933, 2874, 2794, 2779, 2737, 2578, 2490, 2416, 1730, 1633, 1556, 1471, 1433, 1367, 1329, 1163, 1249, 1226, 1192, 1147, 1068, 1045, 935, 910, 893, 736, 700, 682, 619, 588; ^{1}H NMR (500MHz, CD$_3$OD): δ (ppm) = 3.71 (s, 6H), 2.70-2.65 (m, 14H), 1.53-1.47 (p, J = 7.5 Hz, 8H), 1.37-1.29 (s, J = 7.5 Hz, 8H), 1.15-1.12 (t, J = 7.0 Hz, 9H), 0.95-0.92 (t, J = 7.0 Hz, 12H).

TMBTA.DIBUA: MP 206°C; FT-IR (KBr pellet, cm^{-1}): 2964, 2875, 2783, 2271, 2733, 2559, 2455, 1950, 1865, 1840, 1708, 1612, 1552, 1469, 1431, 1373, 1321, 1301, 1261, 1232, 1203, 1182, 1124, 1076, 1022, 947, 910, 893, 827, 790, 761, 731, 688, 667, 601, 536, 524, 428; ^{1}H NMR (300MHz, CD$_3$OD): δ (ppm) = 3.67 (s, 6H), 2. 58-2.56 (d, J = 7.0 Hz, 4H), 2.24 (s, 9H), 1.93-1.89 (m, 2H), 0.95-0.92 (d, J = 6.6 Hz, 6H).

TEBTA.DIBUA: m.p. 211 °C; FT-IR (KBr pellet, cm^{-1}): 3574, 3454, 3124, 3059, 2966, 2929, 2897, 2872, 1706, 2603, 2495, 2420, 1855, 1784, 1716, 1697, 1680, 1610, 1566, 1489, 1464, 1456, 1433, 1392, 1371, 1344, 1311, 1257, 1232, 1219, 1192, 1165, 1085, 1068, 1043, 1030, 964, 933, 898, 839, 812, 754, 723, 696, 677, 619, 588, 553, 522, 447; ^{1}H NMR (500MHz, CD$_3$OD): δ (ppm) = 3.71 (s, 6H), 2.71-2.65 (m, 10H), 1.96-1.93 (m, 2H), 1.25-1.09 (t, J = 7.5 Hz, 6H), 0.97-0.96 (d, J = 6.5 Hz, 12H).

TMBTA.DSBUA: m.p. 234 °C; FT-IR (KBr pellet, cm^{-1}): 3649, 3587, 3441, 3421, 3406, 3385, 3335, 3319, 3298, 3279, 3037, 2972, 2943, 2881, 2744, 2598, 2482, 2148, 1940, 1716, 1674, 1626, 1558, 1489, 1456, 1375, 1311, 1261, 1232, 1190, 1138, 1109, 1078, 1020, 1003, 976, 954, 937, 885, 827, 779, 726, 682, 663, 624, 601, 534, 507; ^{1}H NMR (500MHz, CD$_3$OD): δ (ppm) = 3.66 (s, 6H), 3.11-3.05 (m, , 2H), 2.24 (s, 9H), 1.71- 1.63 (m, 3H), 1.39-1.32 (m, 3H), 1.17-1.16 (d, J = 6.5 Hz, 6H), 0.94-0.91 (t, J = 8, 6H).

TEBTA.DSBUA: m.p. 231 °C; FT-IR (KBr pellet, cm^{-1}): 3574, 3454, 3124, 3059, 2966, 2929, 2897, 2872, 2706, 2603, 2495, 2420, 1855, 1784, 1716, 1697, 1680, 1610, 1566, 1489, 1462, 1454, 1421, 1392, 1336, 1255, 1219, 1192, 1087, 1070, 1043, 970, 933, 902, 829, 781, 752, 723, 675, 659, 621, 590, 553, 522, 445; ^{1}H NMR (500MHz, CD$_3$OD): δ (ppm) = 3.71 (s, 6H), 3.14-3.10 (m, 2H), 2.71-2.67 (q, J = 7.0 Hz, 9H), 1.72-1.67 (m, 3H), 1.40-1.34 (m, 3H), 1.18-1.17 (d, J = 6.5 Hz, 6H), 1.12-1.09 (t, J = 7.5 Hz, 9H), 0.95-0.92 (t, J = 7.5, 6H).

TMBTA.DHA: m.p. 245 °C; FT-IR (KBr pellet, cm^{-1}): 3668, 3605, 3580, 3539, 3518, 3377, 3358, 3333, 3321, 2956, 2931, 2858, 2793, 2740, 2544, 2465, 2359, 2339, 1631, 1568, 1554, 1467, 1371, 1325, 1257, 1220, 1064, 1020, 952, 908, 829, 798, 763, 727, 678, 605; ^{1}H NMR (500MHz, CD$_3$OD): δ (ppm) = 3.64 (s, 6H), 2. 69-2.68 (t, J = 6.5 Hz, 12H), 2.24 (s, 9H), 1.52 (broad s, 8H), 1.30 (broad s, 36H), 0.92-0.91 (t, J = 7.5 Hz, 18H).

TEBTA.DHA: m.p. 253 °C; FT-IR (KBr pellet, cm^{-1}): 3419, 3412, 2958, 2931, 2872, 2858, 2793, 2756, 2742, 2447, 1629, 1558, 1489, 1464, 1458, 1369, 1329, 1263, 1184, 1087, 1068, 1043, 935, 910, 754, 727, 686; ^1H NMR (500MHz, CD_3OD): δ (ppm) = 3.65 (s, 6H), 2.70-2.67 (t, *J* = 6.5 Hz, 12H), 1.53 (broad s, 8H), 1.33 (broad s, 36H), 1.14-1.11 (t, *J* = 7.5 Hz, 18H), 0.90-0.89 (t, *J* = 6.5 Hz, 18H).

TMBTA.DAA: m.p. 214 °C, FT-IR (KBr pellet, cm^{-1}): 3271, 3086, 2985, 2783, 2590, 2459, 2351, 2339, 2320, 2096, 1867, 1732, 1714, 1693, 1645, 1568, 1556, 1531, 1446, 1417, 1371, 1336, 1267, 1234, 1201, 1161, 1078, 1022, 993, 933, 887, 827, 808, 727, 661, 599, 565, 540, 466; ^1H NMR (500MHz, CD_3OD): δ (ppm) = 5.81-5.73 (m, 2H), 5.4 -5.36 (m, 4H), 3.71 (s, 6H), 3.30-3.27 (m, 4H), 2.24 (s, 9H), 0.94-0.91 (t, *J* = 7.5 Hz, 12H).

TEBTA.DAA: m.p. 220 °C, FT-IR (KBr pellet, cm^{-1}): 2966, 2929, 2872, 2831, 2686, 2654, 2617, 2588, 2567, 2459, 1716, 1687, 1616, 1570, 1485, 1456, 1423, 1369, 1313, 1255, 1230, 1192, 1165, 1107, 1085, 1068, 1045, 1018, 993, 933, 898, 829, 717, 665, 651, 592, 553, 453; ^1H NMR (500MHz, CD_3OD): δ (ppm) = 5.81-5.73 (m, 2H), 5.39-5.35 (m, 4H), 3.71 (s, 6H), 3.30 - 3.25(m, 4H), 2.67-2.64 (q, *J* = 7.0 Hz, 9H), 1.13- 1.11 (t, *J* = 7.5 Hz, 12H).

Crystal Structures of the Free Acids.

TMBTA. Diffraction quality single crystals of **TMBTA** were harvested from a mixture of ethanol, ethyl acetate, and hexane. It crystallized in the centrosymmetric monoclinic space group $P2_1/n$. The asymmetric unit contained one molecule of **TMBTA** and half a molecule of ethanol as solvent. The terminal methyl group and the hydroxyl group of the ethanol molecule were found to be disordered over two positions and the whole molecule was further disordered around a centre of inversion. The carboxymethyl arms of the acid moiety adopted *syn-syn-anti* conformation. The torsion angles involving the carboxylmethyl arms and the aromatic ring were calculated to be 93.2, 98.1 and 100.8°, respectively. All the carboxylic acid –OH displayed *syn* conformation. In the crystal structure, **TMBTA** molecule held three neighbouring acid molecules via O-H•••O interactions [O•••O = 2.661(5)-2.698(4) Å; ∠O-H•••O = 168.8-176.2°] displaying typical carboxylic acid dimer. Such hydrogen bonding ultimately lead to the formation of 1D tape architecture having cavities that were occupied by the disordered solvent molecules; such 1D tapes were packed in parallel fashion (Fig.1A-B).

TEBTA. The single crystals of **TEBTA**, suitable for the X-ray diffraction study were grown from a methanol and ethyl acetate solvent mixture. It was found to be isomorphous with **TMBTA** displaying identical space group ($P2_1/n$) and near identical cell dimensions. The asymmetric unit contained a molecule of **TEBTA**. Installation of comparatively more bulky ethyl groups in the place of methyl did not affect the conformation of the carboxymethyl groups relative to the aromatic ring. Thus, **TEBTA** also adopted *syn-syn-anti* conformation. The relative orientation of the carboxylmethyl moieties with respect to the aromatic ring as revealed from the corresponding dihedral angels of 92.8, 97.8 and 108.7° was similar to that observed for **TMBTA**. In this case also, -OH of the COOH moieties adopted *syn* conformation and each one of them displayed typical hydrogen bonded carboxylic acid dimer synthon sustained by O-H•••O interactions [O•••O = **2**.649(9)-2.679(8) Å; ∠O-H•••O = 121.2-165.6°]. Such interactions led to the formation 1D hydrogen bonded tapes similar to that observed in **TMBTA**. Interestingly, the cavities within the 1D hydrogen bonded tape remained unoccupied. Such 1D tape was found to be packed in parallel fashion resulting in an overall open-framework structure (Fig.1C-D).

Crystal Structures of the Salts.

TMBTA.DCHA. The isolated salt **TMBTA.DCHA** was subjected to FT-IR wherein disappearance of $\nu_{C=O}$ for the parent acid at 1697 cm^{-1} and appearance of a new band at around 1610 cm^{-1} suggested complete deprotonation and formation of 1 : 3 (acid : amine) salt. The single crystals of **TMBTA.DCHA** were grown from toluene. It crystallized in the non-centrosymmetric orthorhombic space group Fdd2. The C-O bond distances were found to be within the range of 1.241(3)-1.255(2) Å indicating the deprotonation of all the three carboxylic acid groups which corroborated well with the FT-IR data. The asymmetric unit contained one carboxylate moiety, three dicyclohexyl ammonium cation and one water molecule. The carboxymethyl groups displayed *syn-syn-anti* conformation as observed in the crystal structure of its parent acid. The dihedral angles involving the carboxymethyl groups and the aromatic ring were found to be 92.2, 92.4 and 94.5° which were quite different from its free acid. This could be because of the various hydrogen bonding interactions involving the COO$^-$ and ammonium cations. In fact, various hydrogen bonding of the type N-H•••O and O-H•••O interactions governed the crystal structure; each tricarboxylate moiety was found to be holding five ammonium cations via N-H•••O interactions [O•••N = 2.674(3)-3.107(3) Å; ∠O-

H•••N = 130.8-172.3°]. The solvent water molecule was involved in hydrogen bonding with the two neighbouring COO^- via O-H•••O interactions [O•••O = 2.748(4)-2.827(3) Å; ∠O-H•••O = 151(3)-156(4)°]. The overall hydrogen bonded network was found to be 3D (Fig.2A-B).

TEBTA.DCHA. On the other hand, the FT-IR of the isolated salt **TEBTA.DCHA** displayed the presence of 1564 cm^{-1} band which was attributed to $\nu_{C=O}$ of COO^- ; absence of $\nu_{C=O}$ for COOH at 1699 cm^{-1} for the parent acid confirmed complete deprotonation and formation of 1 : 3 (acid : amine) salt **TEBTA.DCHA**. Single crystals of the salt were grown from 1,4-dioxane and methanol mixture. It crystallised in the centrosymmetric monoclinic space group $P2_1/n$. The asymmetric unit contained one mono-anionic acid moiety, one ammonium moiety and one water molecule. Further examination showed that only one of the three COOH groups of the acid moiety was deprotonated as revealed from the C-O bond distances [1.1914(17)-1.3096(16) Å; 1.2155(15)-1.3165(14) Å for COOH and 1.2682(15)-1.2393(14) Å for COO^-]. Thus, it was clear that upon crystallization, the salt **TEBTA.DCHA** crystallized out as 1 : 1 monohydrate salt. In this case also, the carboxymethyl groups displayed *syn-syn-anti* conformation; the ethyl substituents also displayed the same conformation. The torsion angles involving the carboxylmethyl arms and the aromatic ring were 94.4°, 97.7° and 98.0°. While –OH of one COOH adopted *anti* conformation, the other one showed *syn*. In the crystal structure, the COOH and COO^- moieties of the adjacent monoanions formed a 1D hydrogen bonded chain [O-H•••O = 2.5572(12) Å; ∠O-H•••O = 163.6°]; the ammonium cation was located within such chain sustained by N-H•••O hydrogen bonding [O•••N = 2.7630(13)-2.8101(13) Å; ∠O-H•••N = 156.6-164.2°] with the COOH and COO^- of the same acid moiety. Such 1D chains were arranged in parallel fashion sustained by O-H•••O [O•••O = 2.5698(14)-2.7713(14) Å; ∠O-H•••O = 165.1(18)-177.7°] hydrogen bonding interactions involving the solvent water molecules resulting in an overall 2D hydrogen bonded layer structure that packed in parallel fashion (Fig.2C-D).

TMBTA.DPA. In **TMBTA.DPA**, $\nu_{C=O}$ for both COOH (1701 cm^{-1}) and COO^- (1585 cm^{-1}) were present in the FT-IR of the isolated salt indicating the acid and the amine did not react in desired 1 : 3 molar ratio. The single crystals of the salt were harvested from isopropanol. It crystallised in the centrosymmetric monoclinic space group $P2_1/c$. The asymmetric unit contained one ion-pair wherein the dipropylammonium (**DPA**) cation was found to be disordered. The fact that only one of the three COOH groups was deprotonated was evident from the corresponding C-O bond lengths [1.209(5)-1.289(5) Å; 1.223(4)-1.308(4) Å for COOH and 1.218(4)-1.281(4) Å for COO^-] indicating the formation of 1 : 1 salt. Interestingly, all the carboxymethyl arms were oriented in *syn-syn-syn* conformation. The torsion angles involving the carboxymethyl arms and the aromatic ring were 92.2, 92.4 and 92.8°. Both *syn* and *anti* conformation were observed for the –OH of the two COOH groups. The monoanions were self-assembled via COO^-•••HOOC hydrogen bonding [O•••O = 2.553(4)-2.639(5) Å; ∠O-H•••O = 168.8-174.2°] resulting in a 2D hydrogen bonded sheet architecture. The disordered **DPA** units were found to be intercalated within two such parallel 2D sheets sustained via N-H•••O interactions [2.771-2.848 Å] involving the ammonium cation and carboxylic moieties resulting in 2D layered hydrogen bonded network. Such 2D networks were further packed in parallel fashion sustained by π-π stacking (4.04 Å) interactions (Fig.3A-B).

TEBTA.DPA. FT-IR of the isolated salt **TEBTA.DPA** showed bands at 1703 and 1562 cm^{-1} which indicated the presence of both COOH and COO^- suggesting incomplete deprotonation of COOH groups.

Diffraction quality single crystals of the salt were grown from methanol. It crystallized in the non-centrosymmetric monoclinic space group $P2_1/c$. The asymmetric unit contained two ion pair compriseds of monoanionic acid moieties and dipropyl ammonium (**DPA**) cations. The fact that two of the three COOH groups in each moiety remained protonated was evident from the C-O bond distances [1.202(6)-1.314(6) Å; 1.215(6)-1.304(6) Å for COOH and 1.226(6)-1.281(6) Å for COO^-]. These data clearly indicated that **TEBTA.DPA** was a 1 : 1 salt and In this salt, both ethyl and carboxymethyl moieties displayed *syn-syn-syn* conformation; however, the relative orientation of the ethyl and carboxymethyl was anti. The torsion angles involving the carboxymethyl arms and the aromatic ring were -90.00- 90.56°, -92.95°- - 95.77-and -93.48-92.75°, respectively. The –OH of the COOH groups displayed both *anti* and *syn* conformation. The monoanions were self-assembled to form 2D hydrogen bonded sheet sustained by O-H•••O [O•••O = 2.520(5)- 2.582(5) Å; ∠O-H•••O = 164.8°-173.2°] interactions involving the COOH and COO^- moieties. Such 2D sheets were further packed in parallel fashion bridged by the ammonium cations that displayed N-H•••O [O•••N = 2.765(7)-2.798(7) Å; ∠O-H•••N = 152.8-165.3°] interactions with various O atoms of the COOH/COO^- moieties of the interacting 2D sheets resulting in 2D layered structure. Since the ethyl groups were oriented opposite to the carboxymethyl arms, no π-π stacking interactions could be observed although the 2D layered structures were packed in parallel fashion (Fig.S1).

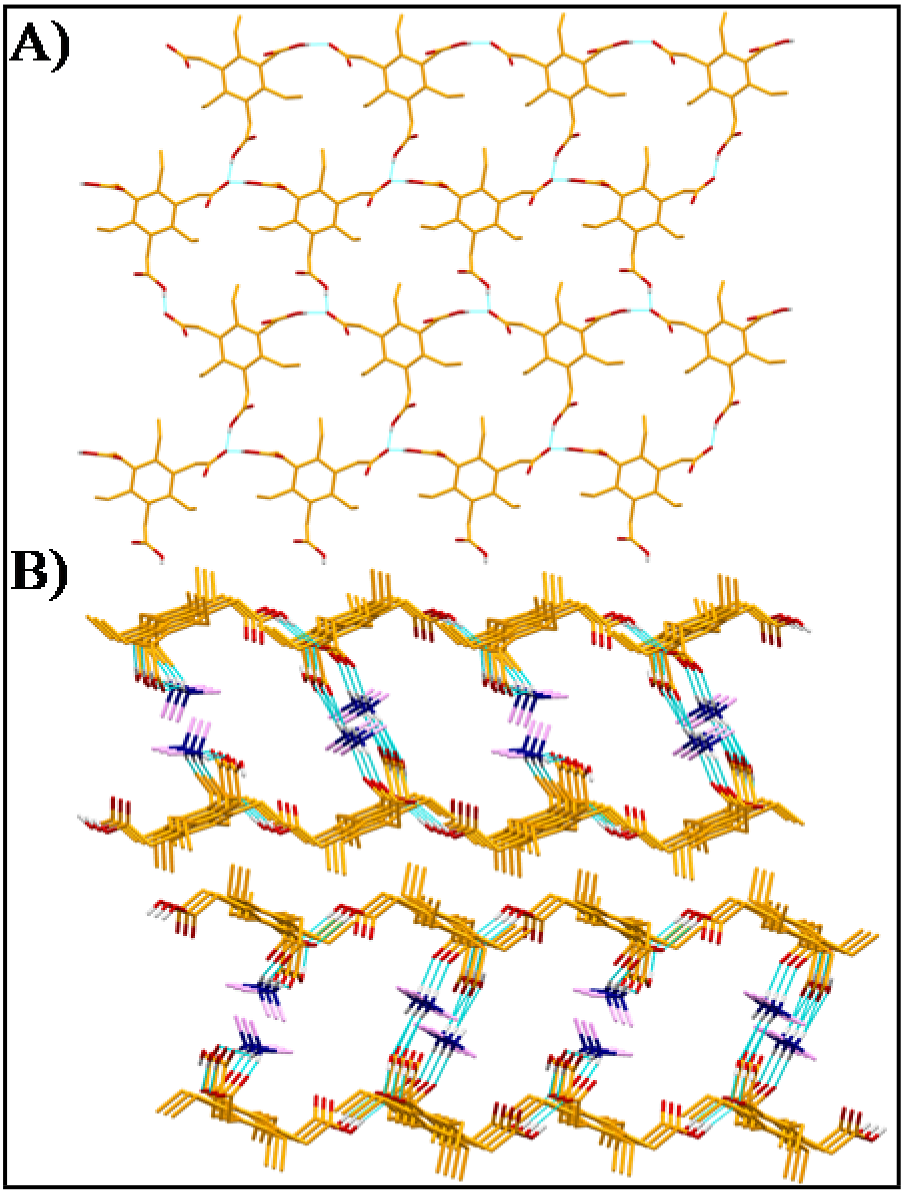


Fig.S1. Crystal structure illustration of **TEBTA.DPA**; A) 2-D hydrogen bonded sheet involving the anionic moieties; B) parallel packing of the 2-D layered structure.

TMBTA.DIBUA. The salt **TMBTA.DIBUA** showed two bands at 1708 and 1552 cm^{-1} in its FT-IR spectrum which indicated the presence of both COOH and COO^{-} in the synthesized solid. The single crystals suitable for the diffraction study were grown from methanol, which crystallised in the centrosymmetric monoclinic space group $P2_1/c$. The asymmetric unit contained one acid moiety and one diisobutylammonium (**DIBUA**) cation. Various C-O bond lengths [1.203(3)-1.293(3) Å for COOH; 1.215(2)-1.314(2) and 1.234(2)-1.272(2) Å for COO^{-}] present in the crystal structure clearly established the monoanionic nature of the acid moiety. The carboxymethyl groups displayed *syn-syn-syn* conformation. The torsion angles involving the carboxymethyl groups and the aromatic rings were found to be 94.0, 97.9 and 98.5º respectively. The relative orientation of the carboxylic acid protons were found be *syn* and *anti*. The monoanionic species were self-assembled via O-H•••O [O•••O = 2.575(2) Å-2.578(2) Å; ∠O-H•••O = 161.2°-164.9°] interactions involving the COOH and COO^{-} moieties resulting in 2D sheet architecture. The cationic species were located within the interstitial space between two such 2D sheets sustained by N-H•••O interactions [O•••N = 2.803(2)-2.872(3) Å; ∠O-H•••N = 152.6-171.2°]; in this case, the ammonium cation was found to be involved in hydrogen bonding interactions with COOH and COO$^-$ of the same acid moiety. In the overall packing, the *syn-syn-syn* conformation presumably allowed the 2D sheet to pack further in parallel fashion (Fig.S2) displaying π-π interactions (3.96 Å).

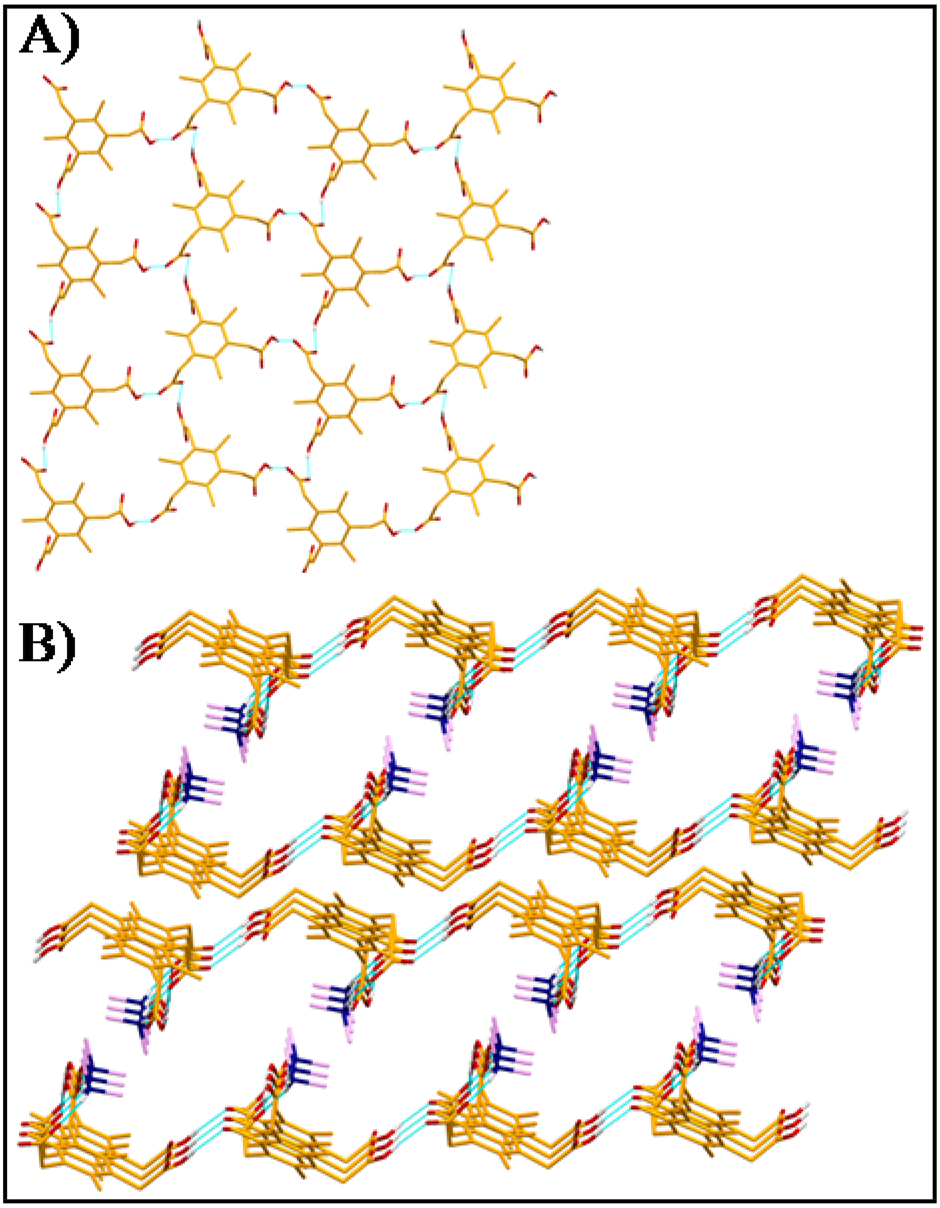


Fig.S2. Crystal structure illustration of **TMBTA.DIBUA**; A) 2-D hydrogen bonded sheet of the anionic species; B) parallel packing of the 2-D layered structures displaying π-π stacking.

TEBTA.DIBUA. The FT-IR of the salt **TEBTA.DIBUA** showed two characteristics bands at 1695 and 1566 cm^{-1} indicating the presence of both the COOH and COO$^-$ in the as synthesized salt. The single crystals were harvested from ethanol and it crystallized in the centrosymmetric monoclinic space group P2$_1$/c. The asymmetric unit contained two **TEBTA** anions and two diisobutyl ammonium cations (**DIBUA**). The C-O bond distances [1.302(4)-1.304(4) Å, 1.196(4)-1.195(4) Å and 1.311(4)-1.312(4) Å, 1.212(4)-1.217(4) Å for COOH; 1.273(4)-1.277(4) Å, 1.220(4)-1.233(4) Å for COO-] present in the crystal structure confirmed the presence monoanionic nature of the acid moieties. The carboxymethyl arms adopted *syn-syn-syn* conformation. The torsion angles involving the carboxymethyl arms and the aromatic ring were 90.9-91.7, 94.5-94.7 and 95.2-97.1°, respectively. The two carboxylic acid protons adopted *syn* and *anti* conformation. In the crystal structure, the monoanionic acid moiety was found to be a 2D sheet like architecture sustained by O-H•••O [O•••O = 2.545(3)-2.637(3) Å and ∠O-H•••O = 168.5-174.5°] interactions. **DIBUA** cations were intercalated between the space formed by the two adjacent 2D sheet and was engaged in the hydrogen bonding interactions with the COO^- and COOH functionality of the same acid moiety involving N-H•••O [O•••N = 2.769(4)-2.796(4) Å and ∠N-H•••O = 150.2-172.2°] interactions. The overall packing did not show any π-π interaction as *syn-syn-syn* conformation of the ethyl groups prevented the π-π stacking interactions (Fig.S3).

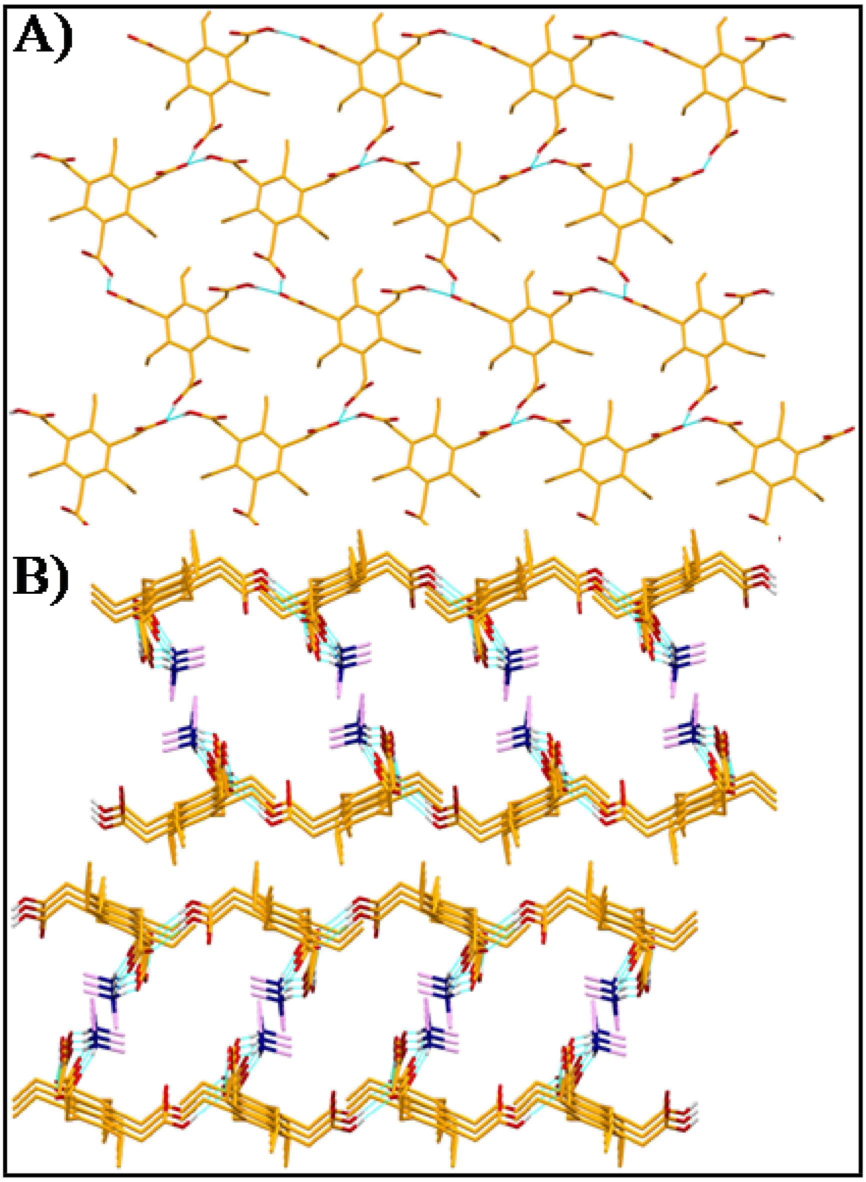


Fig.S3. Crystal structure illustration of **TEBTA.DIBUA**; A) 2-D hydrogen bonded sheet involving the anionic species; B) parallel packing of the 2-D layered structures.

TMBTA.DAA. Two characteristics FT-IR band at 1732 and 1556 cm^{-1} were indicative of the presence both the COOH and COO^- in the salt **TMBTA.DAA**. Crystals suitable for the single crystal X-ray diffraction were grown from methanol and it crystallized in the centrosymmetric monoclinic space group $P2_1/c$. The asymmetric unit contained one **TMBTA** anion and one disordered diallyl ammonium (**DAA)**

cation. The C-O distances [1.209(4)-1.326(3) Å and 1.235(3)-1.317(3) Å for the COOH and 1.223(4)-1.287(3) Å for the COO$^-$] present in the crystal structure supported the fact that the tripodal scaffold contained two COOH and one COO$^-$ groups in the crystalline solid. The three carboxymethyl arms were found to be adopted *syn-syn-syn* conformation. The torsion angles associated with the COOH/COO$^-$ and the phenyl plane were calculated to be 91.2, 92.0 and 95.7° respectively. The two COOH protons were found to be in *syn* and *anti*. The monoanionic acid moiety was found to be self assembled in the crystal lattice via O-H•••O [O•••O = 2.539(3)-2.622(3) Å; ∠O-H•••O = 172.8-173.6°] interactions involving COOH and COO$^-$ resulting into a 2D sheet structure. The **DAA** cations were found to be occupied in the interstitial space between the parallel packed 2D sheets sustained by N-H•••O [N•••O = 2.735(4)-2.815(3) Å; ∠N-H•••O = 166.9-179.4°] interactions with the COOH and COO$^-$ of the acid moiety. Parallel packing of the 2D sheets were also found to be sustained by the π-π (4.0 Å) stacking interactions (Fig.S4).

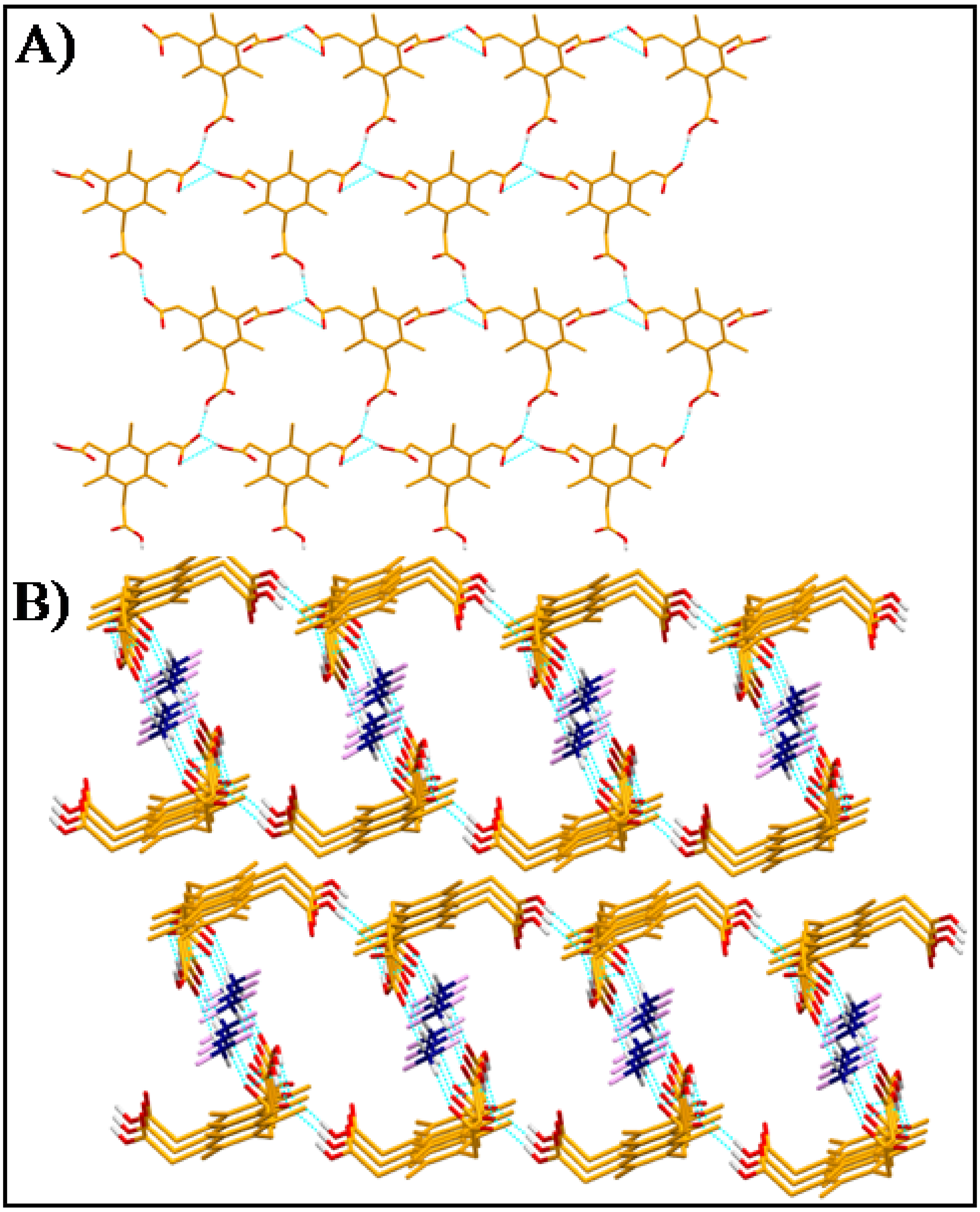


Fig.S4. Crystal structure illustration of **TMBTA.DAA**; A) 2-D hydrogen bonded sheet involving the anions; B) parallel packing of the layered structures. Carbon atoms of the disordered **DAA** cations.

TEBTA.DAA. FT-IR of the salt **TEBTA.DAA** showed two characteristics bands at 1716, 1570 cm^{-1} indicating of the existence of both the COOH and COO^-. The crystals suitable for the single crystal X-ray diffraction were grown from methanol-isopropanol mixture and were found to be crystallised in the non-centrosymmetric orthorhombic space group $Pca2_1$. The asymmetric unit contained two **TEBTA** anions and two disordered diallyl ammonium (**DAA**) cations. The C-O distances [1.317(5)-1.331(5), 1.204(5)-1.205(6) Å and 1.314(5)-1.319(6), 1.216(6)-1.220(6) Å for the COOH and 1.288(5)-1.294(5), 1.215(6)-1.225(5) Å for the COO^-] present in the crystal structure supported the monoanionic nature of the carboxylic moiety. In the monoanionic species, the carboxymethyl arms displayed *syn-syn-syn* conformation and were oriented opposite to the ethyl group. The torsion angles involving the COOH/COO^- and the π-plane were calculated to be 91.6-92.0, 92.4-93.2 and 94.9-96.7° respectively. The COOH groups in each monoanioic species adopted *syn* and *anti* conformation. The monoanionic tripodal acid moieties were self-assembled into a 2D sheet structure sustained by O-H•••O [O•••O = 2.478(4)-2.620(4) Å, ∠O-H•••O = 165.5-174.5°] interactions involving COOH and COO^-. The **DAA** cation was found to be occupying the interstitial space between the parallely packed 2D sheets involving N-H•••O [N•••O = 2.711(5)-3.076(5) Å, ∠N-H•••O = 120.0-174.2°] interactions. Understandably because of the *syn-syn-syn* conformation of the ethyl groups, the 2D sheets could not get involved in π-π stacking interactions (Fig.S5).

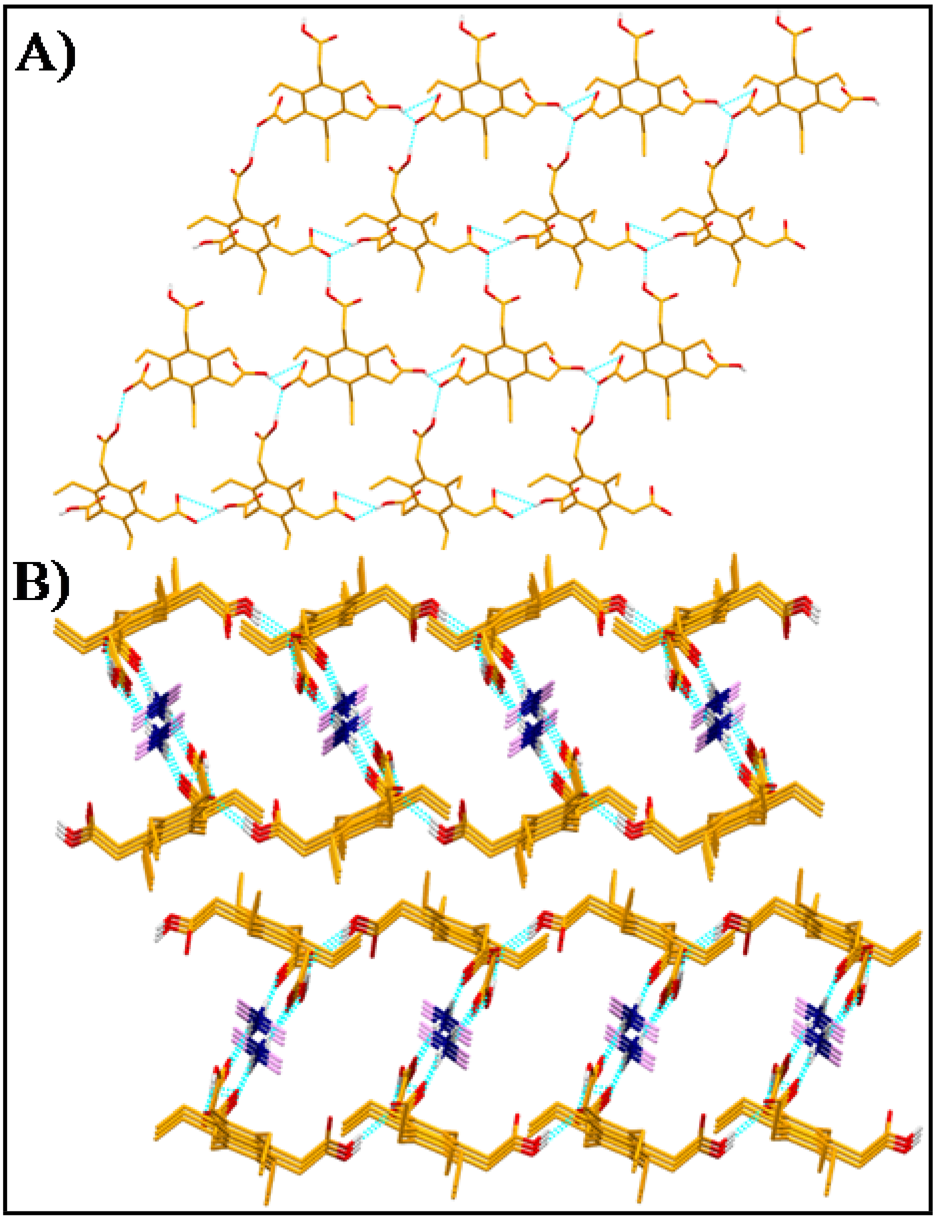
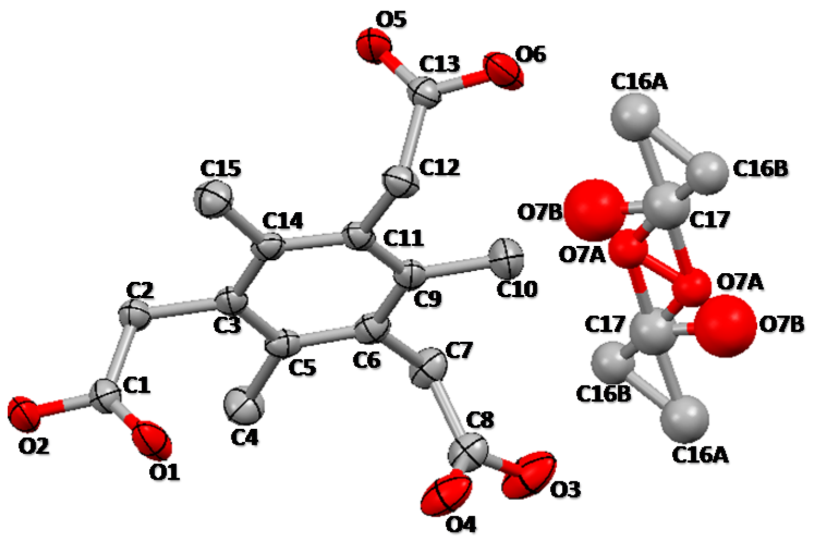


Fig.S5. Crystal structure illustration of **TEBTA.DAA**; A) 2-D hydrogen bonded sheet of the anions; B) parallel packing of the layered structures; carbon atoms of the disordered **DAA** cation.

TMBTA.DSBUA. Two characteristic FT-IR bands at 1716 and 1626 cm^{-1} confirmed the presence of both COOH and COO^{-} in the salt **TMBTA.DSBUA.** The single crystals were grown from ethanol and it crystallized in the non-centrosymmetric monoclinic space group P2$_1$. The asymmetric unit contained one **TMBTA** anion and disecondarybutyl ammonium **(DSBUA)** cation. The various C-O bond distances [1.205(4)-1.289(4) and 1.237(4)-1.287(4) Å for COOH and 1.236(4)-1.284(4) Å for COO^{-}] also supported the incomplete deprotonation of all the acid moieties. Interestingly the carboxymethyl arms of the acid moiety adopted *syn-syn-anti* conformation. The torsion angles between the carboxymethyl arm and the phenyl plane were estimated to be 92.4, 94.6 and 102.2º respectively. The two carboxylic protons were found to be in *syn* conformation. The crystal structure revealed that the monoanionic moiety formed a 2D corrugated sheet structure sustained by O-H•••O [O•••O = 3.187(4)-2.429(4) Å and ∠O-H•••O = 120(4)-159(5)°] interactions. The **DSBUA** cations were located within the interstitial space of the parallel packing of the corrugated sheets sustained by N-H•••O [O•••N = 2.784(4)-2.792(4) Å and ∠N-H•••O = 154.5-171.2°] interactions. (Fig.4A-B).

TEBTA.DSBUA. Characteristics FT-IR bands at 1716 and 1566 cm^{-1} in the salt **TEBTA.DSBUA** were attributed to the $\nu_{C=O}$ of COOH and COO^- respectively. The crystals suitable for single crystal X-ray diffraction were grown from ethanol; they were found to be crystallised in the monoclinic centrosymmetric space group $P2_1/c$. The asymmetric unit contained two **TEBTA** anions, two disordered disecondarybutyl ammonium (**DSBUA)** cations and two solvent water molecules. The various C-O distances [1.209(5)-1.220(6), 1.309(6)-1.318(6) Å and 1.215(5)-1.220(5), 1.288(5)-1.294(5) Å for COOH and 1.189(6)-1.206(6), 1.265(6)-1.283(6) Å for COO^-] supported incomplete deprotonation of all the COOH groups. The hydrogen atom of one of the COOH moiety could not be located in the difference fourier map. The three carboxymethyl arms were found to adopt *syn-syn-syn* conformation. The torsion angles involving the carboxymethyl arms and the phenyl plane were calculated to be 89.9-90.5, 89.8-90.4 and 93.9-94.5°, respectively. The COOH proton in each of the acid moieties were found to be adopting less frequently observed *anti* conformation. The monoanionic acid moiety was found to be self assembled via O-H•••O [O•••O = 2.555(5)-2.573(4) Å; ∠O-H•••O = 171.6-173.7°] interactions leading to the formation of a 2D sheet like architecture in the crystal structure. **DSBUA** cations and the solvent water molecules were located between the two adjacent 2D sheets involving O-H•••O [2.74-2.76 Å] and N-H•••O [N•••O = 2.845(7)-2.885(6) Å; ∠N-H•••O = 163-167°] interactions, respectively. Because of the *syn-syn-syn* conformation of the three ethyl groups, no π-π staking interaction could be observed although the 2D sheets were packed in the parallel fashion (Fig.4C-D).

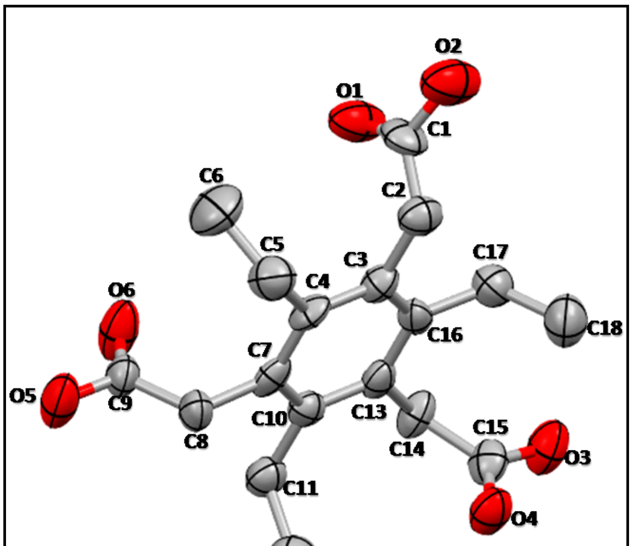
Molecular Plot and Hydrogen Bonding Parameters for Parent Acis and the Salts



Molecular plot of **TMBTA** (ellipsoid with 50% probability).

Hydrogen bonding parameters of **TMBTA**.

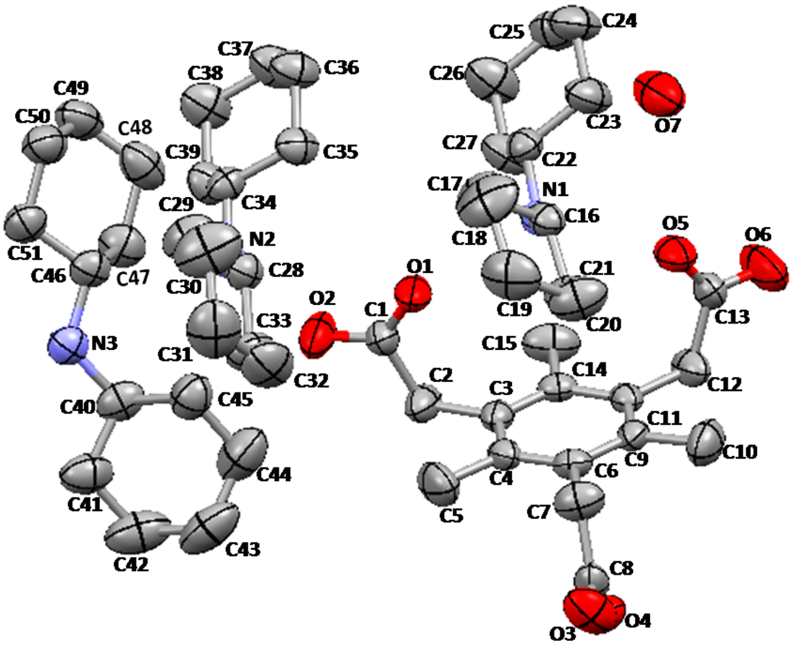
D—H•••A	D—H (Å)	H•••A (Å)	D•••A (Å)	D—H•••A (°)	Symmetry operation for A
O(2)—H(2)•••O(5)	0.82	1.88	2.698(4)	176.2	x+1, y, z
O(3)—H(3)•••O(4)	0.82	1.85	2.661(5)	169.8	-x+2, -y+2, -z



Molecular plot of **TEBTA** (ellipsoid with 50% probability).

Hydrogen bonding parameters of **TEBTA**.

D–H•••A	D–H (Å)	H•••A (Å)	D•••A (Å)	D–H•••A (°)	Symmetry operation for A
O(5)–H(5)•••O(4)	0.82	1.92	2.667(8)	153	x+1, y, z
O(3)–H(3)•••O(6)	0.82	2.16	2.679(8)	121	x-1, y, z
O(2)–H(2)•••O(1)	0.82	1.85	2.649(9)	166	-x+1, -y+1, -z

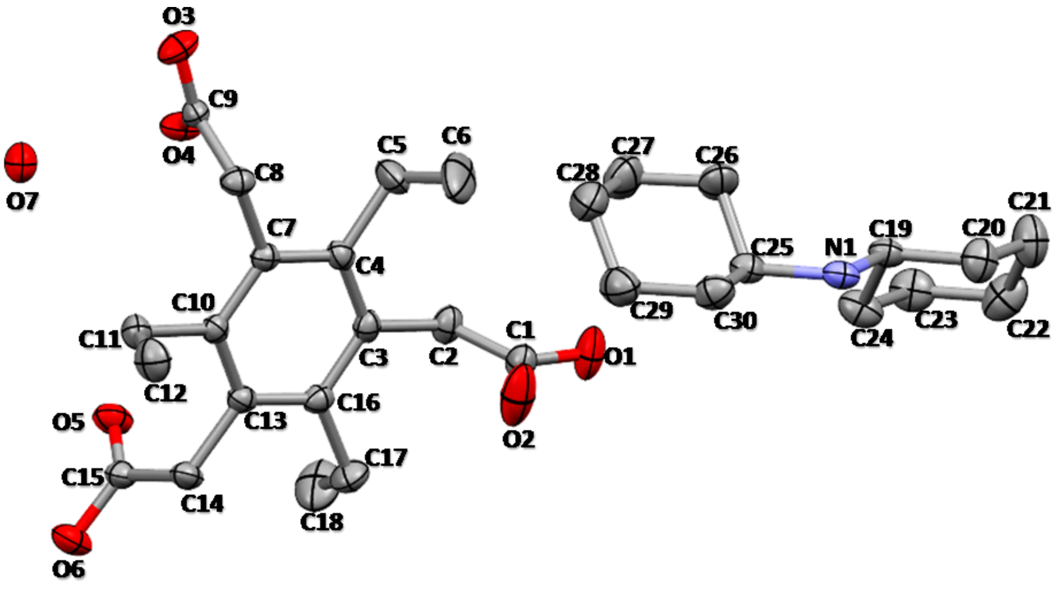


Molecular plot of **TMBTA.DCHA** (ellipsoid with 50%

probability).

Hydrogen bonding parameters of **TMBTA.DCHA**.

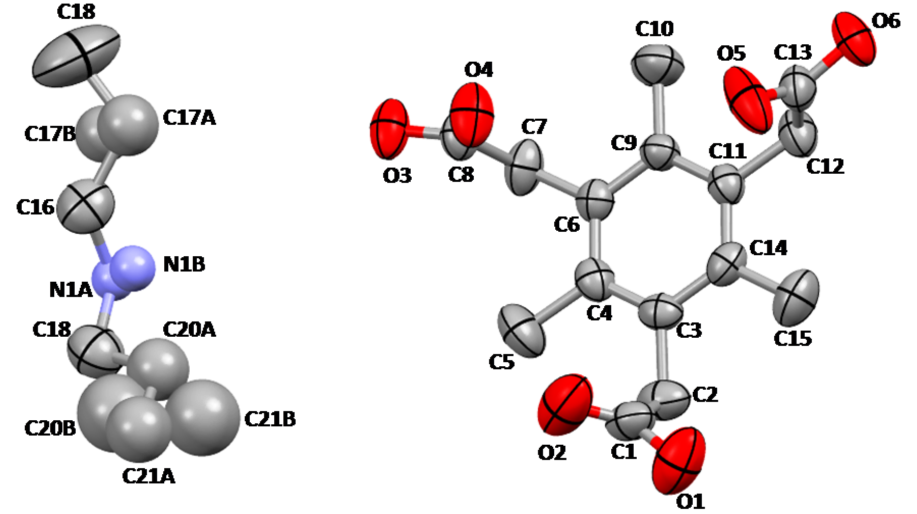
D—H•••A	D—H (Å)	H•••A (Å)	D•••A (Å)	D—H•••A (°)	Symmetry operation for A
N(1)—H(1A)•••O(5)	0.90	1.91	2.782(3)	164	x, y, z
N(1)—H(1B)•••O(1)	0.90	1.89	2.775(2)	169	x, y, z
N(2)—H(2B)•••O(2)	0.90	1.78	2.674(3)	172	x, y, z
N(2)—H(2B)•••O(4)	0.90	1.90	2.774(3)	165	-x+1/2, -y, z-1/2
N(3)—H(3A)•••O(3)	0.90	1.93	2.767(3)	154	-x+1/2, -y, z-1/2
N(3)—H(3B)•••O(5)	0.90	2.22	3.107(3)	169	x+1/4, -y+1/4, z-3/4
N(3)—H(3B)•••O(6)	0.90	2.38	3.042(3)	131	x+1/4, -y+1/4, z-3/4
O(7)—H(7WA)•••O(6)	1.02(4)	1.81(4)	2.748(4)	151(3)	x-1/4, -y+1/4, z-1/4
O(7)—H(7WB)•••O(3)	0.97(6)	1.91(6)	2.827(3)	156(4)	-x+1/4, y+1/4, z+1/4



Molecular plot of **TEBTA.DCHA** (ellipsoid with 50% probability).

Hydrogen bonding parameters of **TEBTA.DCHA**.

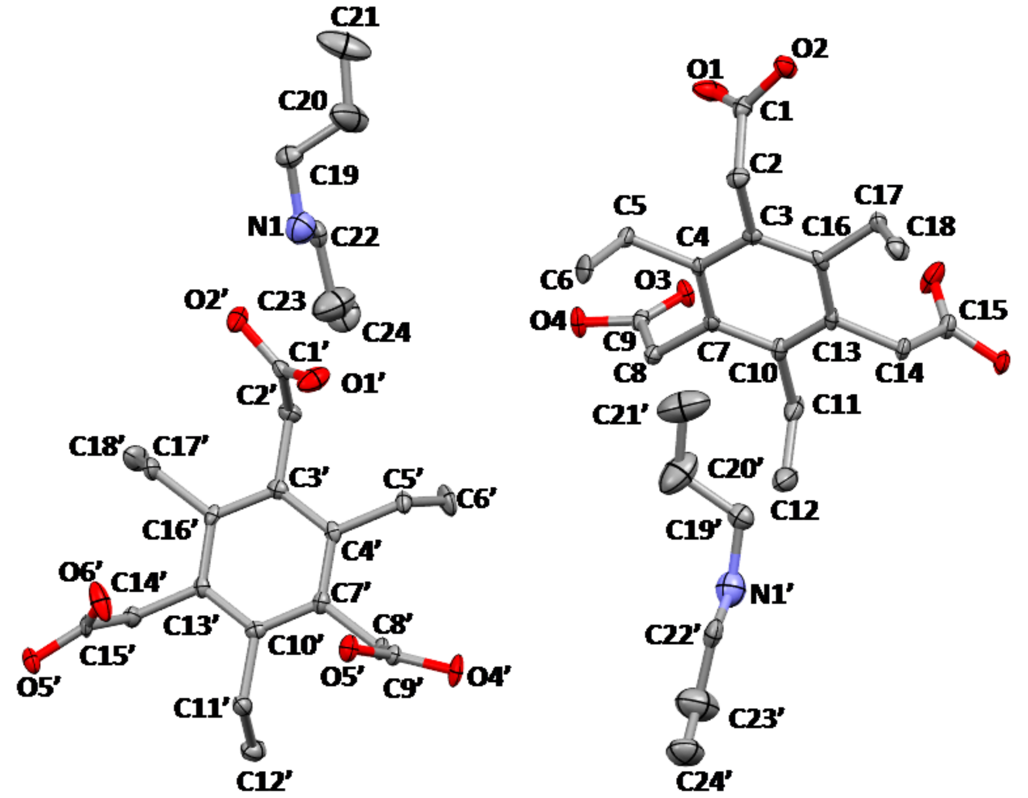
D—H•••A	D—H (Å)	H•••A (Å)	D•••A (Å)	D—H•••A (°)	Symmetry operation for A
O(7)—H(7B)•••O(3)	0.90 (2)	1.87(2)	2.7407(14)	164(2)	-x+3/2, y+1/2, -z+3/2
O(7)—H(7A)•••O(3)	0.91 (2)	1.88(2)	2.7713(14)	165.1(18)	x-1/2, -y+1/2, z+1/2
N(1)—H(1B)•••O(5)	0.90	1.96	2.8101(13)	157	x-1, y, z
N(1)—H(1A)•••O(4)	0.90	1.89	2.7630(13)	164	x-1, y, z
O(6)—H(6)•••O(4)	0.82	1.76	2.5572(12)	164	x, y+1, z
O(2)—H(2)•••O(7)	0.82	1.75	2.5698(14)	178	x, y, z-1



Molecular plot of **TMBTA.DPA** (ellipsoid with 50% probability).

Hydrogen bonding parameters of **TMBTA.DPA**.

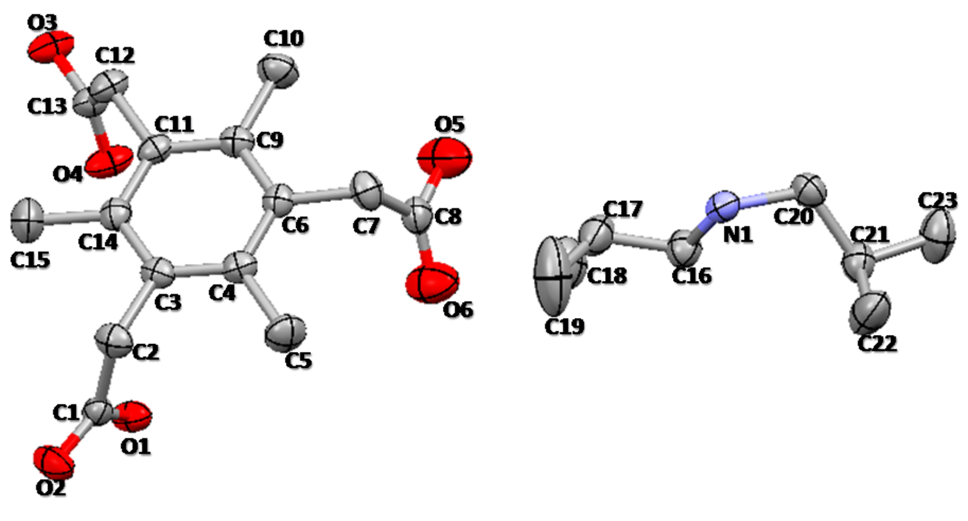
D─H•••A	D─H (Å)	H•••A (Å)	D•••A (Å)	D─H•••A (°)	Symmetry operation for A
O(1)─H(1)•••O(6)	0.82	1.83	2.639(5)	169	x, -y-1/2, z-1/2
O(3)─H(3)•••O(6)	0.82	1.74	2.553(4)	174	x, y+1, z



Molecular plot of **TEBTA.DPA** (ellipsoid with 50% probability).

Hydrogen bonding parameters of **TEBTA.DPA**.

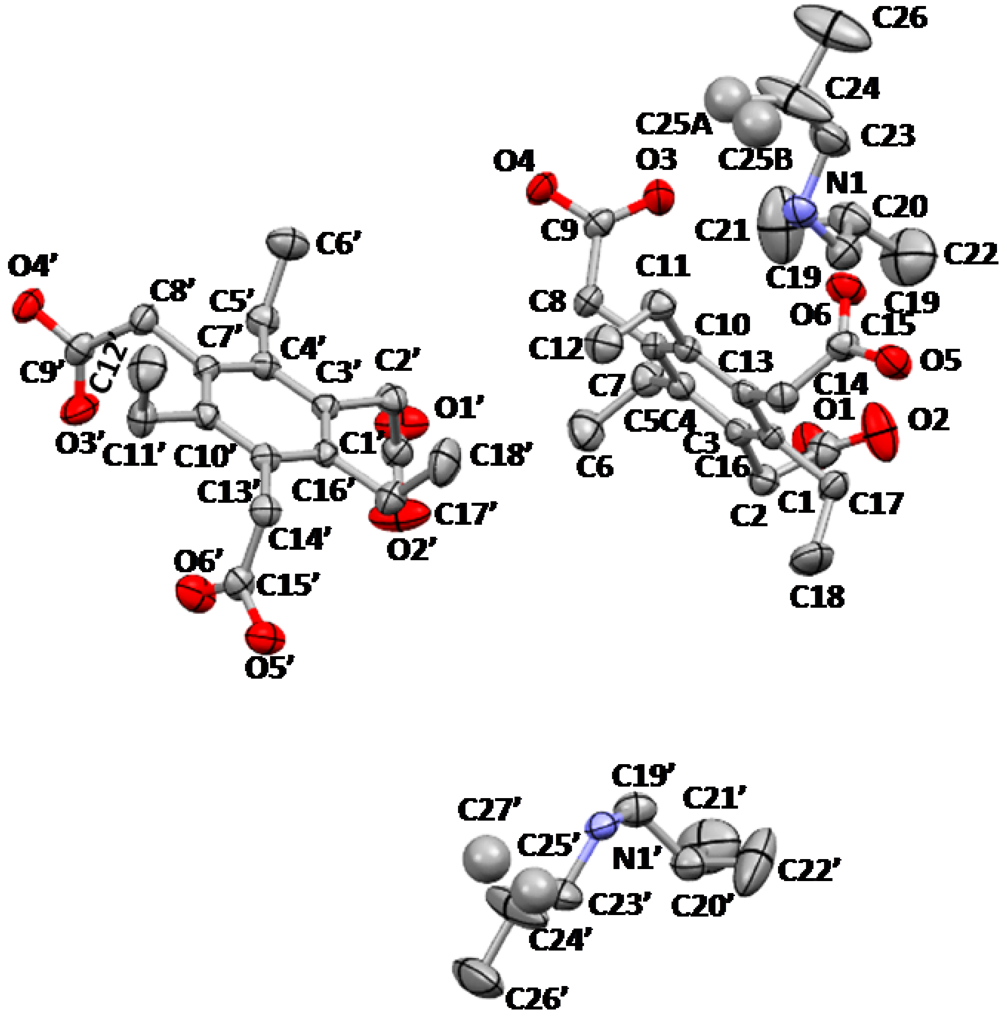
D—H•••A	D—H (Å)	H•••A (Å)	D•••A (Å)	D—H•••A (°)	Symmetry operation for A
O(4)—H(4)•••O(5)	0.82	1.70	2.520 (5)	172	x, y-1, z
O(2')—H2')•••O(5')	0.82	1.77	2.583 (5)	171	*x*, -*y*-1/2, *z*+1/2
O(4')—H(4')•••O(5')	0.82	1.73	2.533 (5)	165	x, y+1, z
N(1')—H(1'1)•••O(3')	0.90	1.95	2.788 (7)	153	x, y-1, z
N(1')—H(1'2)•••O(6')	0.90	1.91	2.785 (7)	164	x, y-1, z



Molecular plot of **TMBTA.DIBUA** (ellipsoid with 50% probability).

Hydrogen bonding parameters of **TMBTA.DIBUA**.

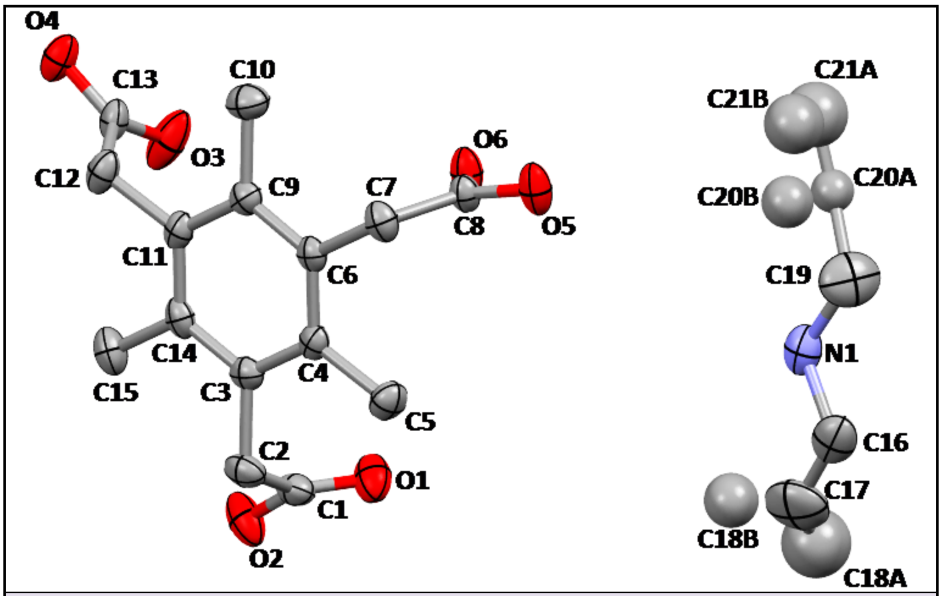
D─H•••A	D─H (Å)	H•••A (Å)	D•••A (Å)	D─H•••A (°)	Symmetry operation for A
O(3)─H(3)•••O(1)	0.82	1.78	2.578(2)	165	x, y-1, z
O(5)─H(5)•••O(2)	0.82	1.79	2.575(2)	161	x, -y+3/2, z-1/2
N(1)─H(1A)•••O(1)	0.90	1.91	2.803(2)	171	x, y, z-1
N(1)─H(1B)•••O(4)	0.90	2.04	2.872(3)	153	x, y, z-1



Molecular plot of **TEBTA.DIBUA** (ellipsoid with 50% probability).

Hydrogen bonding parameters of **TEBTA.DIBUA**.

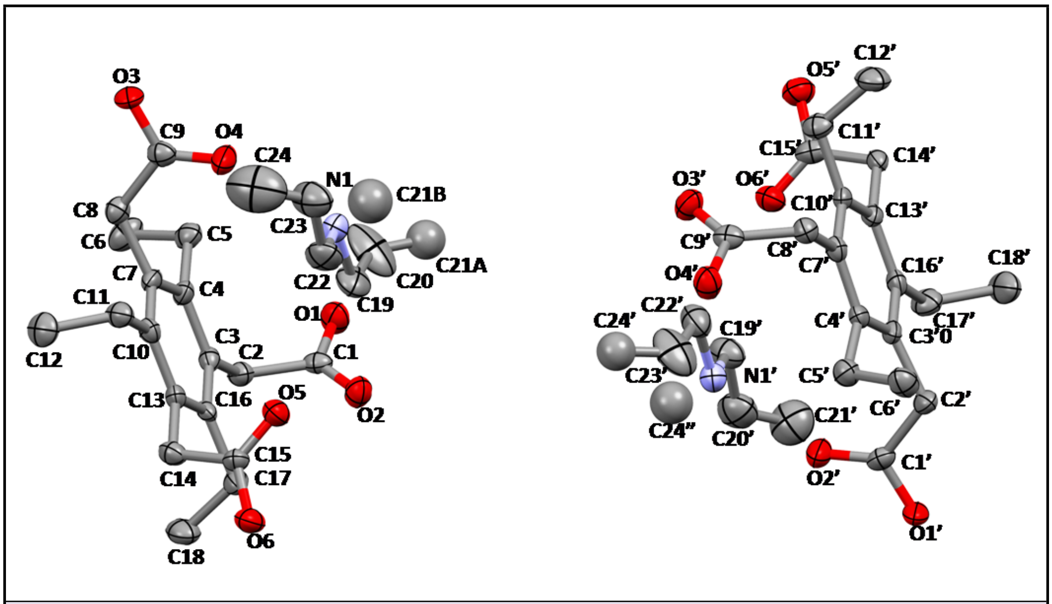
D—H•••A	D—H (Å)	H•••A (Å)	D•••A (Å)	D—H•••A (°)	Symmetry operation for A
N(1')—H(1'2)•••O(3')	0.90	1.90	2.790(4)	172	x, -y+1/2, z+1/2
N(1')—H(1'1)•••O(6')	0.90	1.97	2.796(4)	151	x, -y+1/2, z+1/2
O(5')—H(5')•••O(4')	0.82	1.73	2.545(3)	174	x, y+1, z
O(1')—H(1')•••O(4')	0.82	1.81	2.616(4)	169	x, -y-1/2, z+1/2
N(1)—H(1B)•••O(3)	0.90	1.87	2.769(4)	172	x, y, z
N(1)—H(1A)•••O(6)	0.90	2.00	2.818(4)	150	x, y, z
O(5)—H(5)•••O(4)	0.82	1.75	2.567(3)	175	x, y+1, z
O(1)—H(1)•••O(4)	0.82	1.82	2.637(3)	172	x, -y+1/2, z+1/2



Molecular plot of **TMBTA.DAA**.

Hydrogen bonding parameters of **TMBTA.DAA** (ellipsoid with 50% probability).

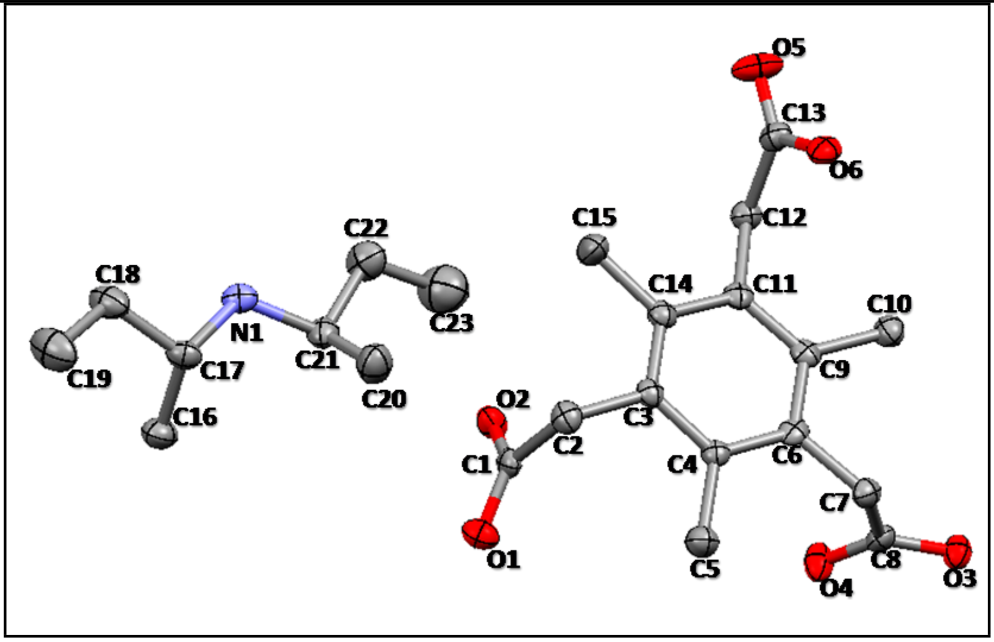
D—H•••A	D—H (Å)	H•••A (Å)	D•••A (Å)	D—H•••A (°)	Symmetry operation for A
N(1)—H(1B)•••O(6)	0.90	1.93	2.815(3)	167	-x+1, y+1/2, -z+1/2
N(1)—H(1A)•••O(3)	0.90	1.83	2.735(4)	179	x, y+1, z
O(5)—H(5)•••O(4)	0.82	1.72	2.539(3)	174	x, y+1, z
O(2)—H(2)•••O(4)	0.82	1.81	2.622(3)	173	x, -y-1/2, z+1/2



Molecular plot of **TEBTA.DAA** (ellipsoid with 50% probability).

Hydrogen bonding parameters of **TEBTA.DAA**.

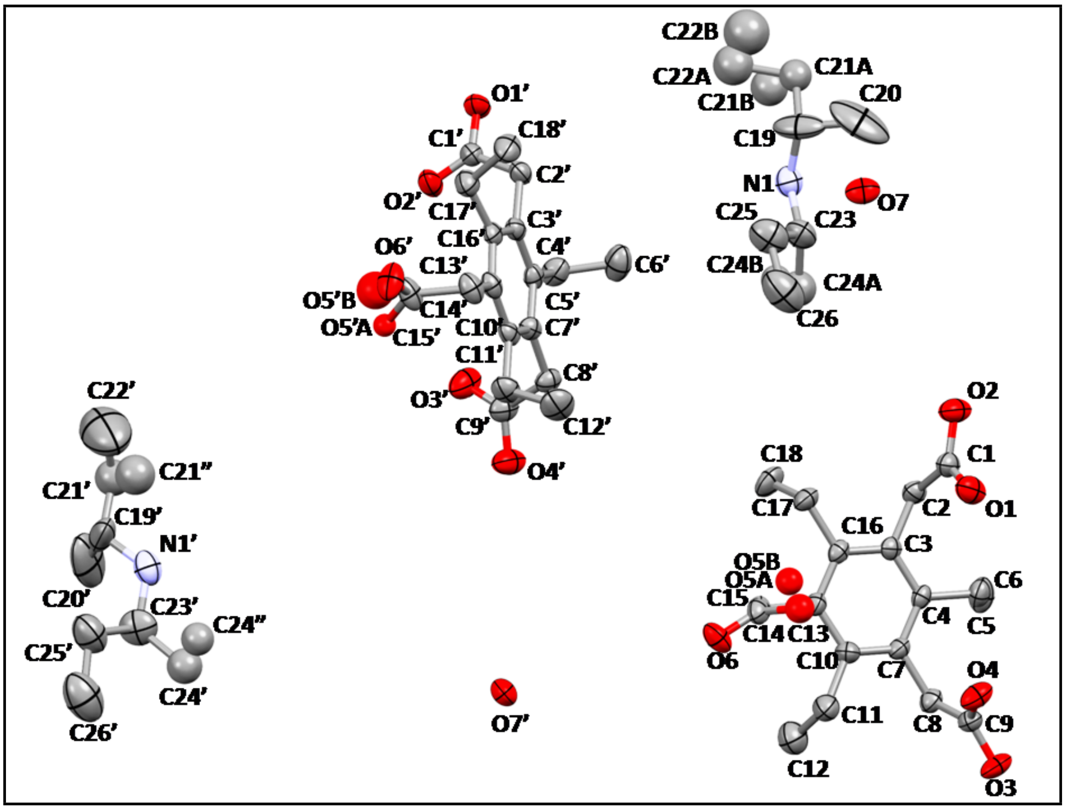
D—H•••A	D—H (Å)	H•••A (Å)	D•••A (Å)	D—H•••A (°)	Symmetry operation for A
N(1’)—H(1’2)•••O(6)	0.90	2.53	3.076(5)	120	x+1/2, -y+1, z
N(1’)—H(1’2)•••O(5)	0.90	1.92	2.807(5)	170	x+1/2, -y+1, z
O(5’)—H(5’)•••O(1’)	0.82	1.68	2.478(4)	166	x, y-1, z
O(4’)—H(4’)•••O(1’)	0.82	1.80	2.610(4)	170	x-1/2, -y+1, z
N(1)—H(1B)•••O(5’)	0.90	2.44	3.016(5)	122	x-1/2, -y, z
N(1)—H(1B)•••O(6’)	0.90	1.97	2.867(5)	173	x-1/2, -y, z
N(1)—H(1A)•••O(4)	0.90	1.81	2.711(5)	175	x, y, z
O(6)—H(6)•••O(3)	0.82	1.69	2.502(4)	173	x, y+1, z
O(1)—H(1)•••O(3)	0.82	1.80	2.620 (4)	175	x+1/2, -y, z



Molecular plot of **TMBTA.DSBUA** (ellipsoid with 50% probability).

Hydrogen bonding parameters of **TMBTA.DSBUA**.

D—H•••A	D—H (Å)	H•••A (Å)	D•••A (Å)	D—H•••A (°)	Symmetry operation for A
O(6)—H(6)•••O(3)	0.89 (6)	2.65(6)	3.187(4)	120(4)	-x+1, y+1/2, -z
O(6)—H(6)•••O(4)	0.89 (6)	1.65(6)	2.528(4)	169(5)	-x+1, y+1/2, -z
O(2)—H(2)•••O(3)	1.09 (6)	1.39(5)	2.429(4)	159(5)	x, y, z+1
N(1)—H(1B)•••O(1)	0.90	1.90	2.792(4)	171	x-1, y, z
N(1)—H(1A)•••O(5)	0.90	1.94	2.784(4)	155	-x, y−1/2, -z+1



Molecular plot of **TEBTA.DSBUA** (ellipsoid with 50% probability).

Hydrogen bonding parameters of **TEBTA.DSBUA**.

D─H•••A	D─H (Å)	H•••A (Å)	D•••A (Å)	D─H•••A (°)	Symmetry operation for A
O(2)─H(2)•••O(3)	0.82	1.76	2.573(4)	174	x, y+1, z
N(1)─H(1A)•••O(5)	0.90	2.01	2.885(6)	163	x, y+1, z
N(1)─H(1B)•••O(7)	0.90	1.86	2.748(5)	168	x, y, z
O(4’)─H(4’)•••O(1’)	0.82	1.74	2.555(5)	172	x, y-1, z
N(1’)─H(1’2)•••O(7’)	0.90	1.86	2.748(6)	170	x, -y+1/2, z-1/2
O(2)─H(2)•••O(3)	0.82	1.76	2.573(4)	174	x, y+1, z
N(1)─H(1A)•••O(5B)	0.90	2.01	2.885(6)	163	x, y+1, z
N(1)─H(1B)•••O(3)	0.90	1.86	2.748(5)	168	x, y, z