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X-ray structures of organic salts between diethanolamine and *ortho*- and *para*-isomers of aminobenzoic acid: A specific synthon responsible for an association of the components

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RESEARCH ARTICLE

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ABSTRACT

Two organic salts between diethanolamine (DEA) and ortho- and para-isomers (OABA and PABA) of aminobenzoic acid (ABA) have been obtained and their X-ray single crystal structures determined. In both salts, cationic and anionic components are incorporated into dimers by the two H-bonds formed between ABA carboxylate oxygen atoms and nitrogen and one of oxygen atoms of DEA which close a cycle with the graph-set notation of $R_2^2(9)$. Further dimers are associated by intricate systems of the H-bonds into 1D- and 3D-network structures in crystals of DEA·OABA and DEA·PABA, respectively. H-bonding which generates these dimers may be considered as a synthon specific for yielding of salts between DEA and mono-substituted aromatic benzoic acids.

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1. Introduction

Ethanolamines are used in an industry as adhesives, antistatic agents, a corrosion inhibitor in metal-cutting fluids and as an ointment emulsifier [1]. They are characterized by low biological activity as antimicrobial [2] and growth stimulating compounds [3]. Benzoic acids are used in a pharmaceutical industry and as conservant and catalyst precursors beyond other applications [4]. They demonstrate moderate antimicrobial [5] and growth stimulating [6,7] activities. Biological activity of ethanolamines may be enhanced through a coordination complex formation, especially with the participation of the benzoic acids as auxiliary ligands yielding mixed-ligand metal complexes. However, ethanolamines easily form chelated metal complexes and may inhibit an involvement of the not chelating auxiliary ligands to coordination sphere [8-10].

Therefore, an alternative way for bioactivity enhancing is a preparation of organic salts between ethanolamines and benzoic acids which is a simpler and very promising approach. Thus, salts of ethanolamines with monosubstituted benzoic acids such as amino-, hydroxy- and nitrobenzoic acids have been synthesized [11] and on example of monoethanolamine salt of *p*-aminobenzoic acid (PABA) an essential enhancement of growth stimulating activity has been demonstrated [12]. Requirements of charge compensation and molecular recognition in the crystalline state lead to an association of the cationic and anionic components into supramolecular units. In crystal engineering of organic salts specific synthons are responsible for such association. In salts of monoethanolamine with monosubstituted benzoic acids protonated ethanolamine molecules are H-bound to benzoic acid molecules through carboxylate groups closing cycles with a graph-set notation of $R_2^2(9)$ [13,14] which may serve as a specific synthon [15].

Nevertheless, relevant organic salts of diethanolamine (DEA) are not obtained except of salt with *p*-nitrobenzoic acid. It is of a great interest to assess which synthons are responsible for an association of components in salts of DEA.

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Table 1. Main crystallographic data and refinement results for compounds DEA·OABA and DEA·PABA.

Parameter	DEA·OABA	DEA·PABA
Empirical formula	$C_4H_{12}NO_2^+$, $C_7H_6NO_2^-$	2($C_4H_{12}NO_2^+$, $C_7H_6NO_2^-$)
Formula weight	242.27	484.54
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a, Å	7.9206(3)	11.0153(3)
b, Å	17.8522(6)	19.7189(5)
c, Å	8.8418(3)	11.4480(2)
β, deg	95.123(3)	93.203(2)
V, Å^3	1245.24(8)	2482.73(10)
Z	4	8
D_x, g.cm^{-3}	1.292	1.294
μ(CuK_α), mm^{-1}	0.823	0.826
T, K	293	293
Scan θ range, deg	4.9-76.1	4.0-76.2
Range h,k,l	-9/9; -22/14; -11/10	-12/13; -24/24; -14/12
Measured reflections	8647	19463
Unique reflections	2557	5145
R_{int}	0.039	0.040
Observed reflections [$F^2 \geq 2\sigma$ (F^2)]	1981	3877
Goodness-of-fit (F^2)	1.04	1.03
R_1, wR_2($I>2\sigma$ (I))	0.0413, 0.1202	0.0503, 0.1483
$\Delta\rho_{min/max}$, eÅ^{-3}	-0.15/0.16	-0.22/0.48

In order to answer this question, we prepared salts of DEA with plant growth stimulator PABA and anthranilic acid, its *o*-isomer (OABA). We report here a preparation and structures of DEA salts with PABA and OABA - DEA·PABA and DEA·OABA, respectively.

2. Experimental

All reagents were readily available from commercial sources and were used as received without further purification. Analyses of C, H and N were performed on a German Elementar Vario EL instrument. Data for the crystal structure determinations were collected at 293 K on an Oxford Diffraction Xcalibur-R CCD diffractometer (CuKα radiation, λ = 1.54184 Å, ω-scan mode, graphite monochromator).

2.1. Preparation of DEA·OABA

To an ethanol solution (5 mL) containing OABA (0.137 g, 1 mmol) DEA (96 μL, 1 mmol) was slowly added with constant stirring. Colorless crystalline product was obtained at 25 °C temperature by solvent evaporation after 15 days. Elemental analysis for $C_{11}H_{18}N_2O_4$ (242.27) - Calculated: C, 54.53; H, 7.49; N, 11.56%. Found: C, 54.64; H, 7.52; N, 11.50%. The yield of the product was 45%. Crystallization experiments were repeated three times and showed the reproducible results.

2.2. Preparation of DEA·PABA

To an ethanol solution (5 mL) containing PABA (0.137 g, 1 mmol) DEA (96 μL, 1 mmol) was slowly added with constant stirring. Colorless crystalline product was obtained at 25 °C temperature by solvent evaporation after 16 days. Elemental analysis for $C_{22}H_{36}N_4O_8$ (484.54) - Calculated: C, 54.53; H, 7.49; N, 11.56%. Found: C, 54.62; H, 7.56; N, 11.48%. The yield of the product was 47%. Crystallization experiments were repeated three times and showed the reproducible results.

2.3. X-ray single crystal structure analysis

The CrysAlisPro program was used for experimental data collection [16]. An absorption correction was applied by the multi-scan method of the same program. The structures were solved by a direct method of the SHELXS-97 program package [17] and refined by full-matrix least squares of the SHELXL-97 program [18]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted at calculated positions and constrained with isotropic thermal parameters, except for the hydrogen atoms of some hydroxyl groups, which were located in a Fourier-difference map and refined isotropically. The molecular drawings were plotted by MERCURY program package [19]. The crystallographic data and details of the structure refinement for both compounds are given in Table 1.

3. Results and discussion

3.1. X-ray single crystal structure of DEA·OABA

There are one OABA and single DEA molecules in an asymmetric part of the monoclinic unit cell (Figure 1). The OABA molecule is in a benzoate form. A fairly strong intramolecular H-bond (Table 2) exists between N1 (donor) and O2 (acceptor) atoms which is denoted by a graph-set notation $S_1^1(6)$ [13,14]. Nevertheless, atoms of the carboxylate group are not rigorously coplanar with atoms of the benzene ring because the dihedral angle between corresponding planes is 13.84°. An aromatic system is nearly parallel to the six-membered cycle O2-C7-C1-C2-N1-H closed due to a formation of the intramolecular H-bond (dihedral angle is 3.55°).

The DEA molecule is in the cationic form because of protonation of the nitrogen atom. It is not in the maximally extended conformation: terminal oxygen atoms are inclined to opposite sides which are featured with the O···O distance of 5.297 Å.

The DEA cation and OABA anion are associated into supramolecular dimers by a pair of relatively strong H-bonds N2-H···O1 and O3-H···O2 (Table 2). These bonds close a cycle with a graph-set notation of $R_2^2(9)$. Further two H-bonds O4-H...O1 related by an inversion center generate tetramers from these dimers (graph-set notation $R_4^4(24)$) (Figure 2a). Incorporation into tetramers is enhanced by relatively weak H-bond C6-H···O4. A pair of the H-bonds N2-H...O3 also related by an inversion center incorporate tetramers into 1D-columns running in the direction of the *a*-axis (Figure 2b). Further these columns are associated into 3D-network by the H-bond N1-H···O4.

The O1 and O2 atoms of the carboxylate groups demonstrate double acceptor properties while protonated N2 atom shows double donor capabilities. Both oxygen atoms of DEA molecules realize donor and acceptor possibilities. The N1 atom is participated in the intra- and intermolecular H-bonds. Thus, all atoms capable to H-bonding participate in H-bonds.

Table 2. H-bonds in DEA·OABA and DEA·PABA.

Bond	Distance, Å			Angle	Coordinates of atom A
D–H···A	D–H	H···A	D···A	D–H···A, °	
DEA·OABA					
N1-H1A···O2	0.92(3)	1.94(3)	2.655(2)	134(2)	-
N1-H1B···O4	0.86(3)	2.30(3)	3.081(2)	151(2)	3/2-*x*, 1/2+*y*, 3/2-*z*
O3-H3···O2	0.882(19)	1.80(2)	2.676(2)	171(2)	-
O4-H4···O1	0.91(3)	1.80(3)	2.708(2)	178(2)	1-*x*, 1-*y*, 2-*z*
N2-H2A···O1	0.93(2)	1.83(2)	2.727(2)	164(2)	-
N2-H2B···O3	0.94(3)	2.06(3)	2.953(2)	158(2)	2-*x*, 1-*y*, 2-*z*
C6-H6··· O4	0.93	2.55	3.124(2)	120	1-*x*, 1-*y*, 2-*z*
DEA·PABA					
O3A-H3A···O2A	0.82	1.76	2.578(2)	176	-
O4B-H4B···O2B	0.80(3)	1.90(3)	2.678(2)	163(3)	-*x*, 1-*y*, 2-*z*
O3B-H3B···O2B	0.89(3)	1.80(3)	2.681(2)	173(4)	-
N2A-H2AA···O1A	0.89	1.91	2.749(2)	157	-
N2B-H2BA···O3A	0.89	1.87	2.757(2)	172	-
N2B-H2BB···O1B	0.89	1.98	2.768(2)	147	-
O4A-H4A···O4B	0.82	2.02	2.843(3)	179	1+*x*, *y*, *z*
N2A-H2AB···O2A	0.89	2.16	3.033(2)	166	1-*x*, 1-*y*, 1-*z*
N1B-H1BA···O1B	0.86	2.27	3.050(3)	154	*x*, 1/2-*y*, 1/2+*z*
N1A-H1AB··· O1A	0.90 (3)	2.14(3)	3.046(3)	176(3)	*x*, 3/2-*y*, -1/2+*z*
N1A-H1AA··· O2B	0.79 (3)	2.26(3)	3.044(3)	173(3)	1-*x*, 1/2+*y*, 3/2-*z*

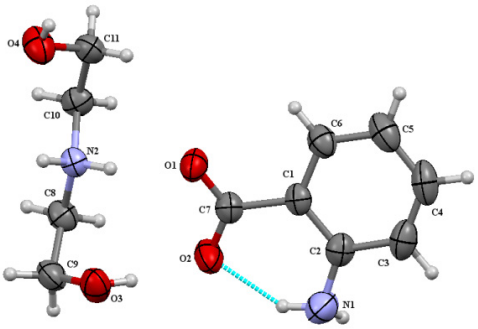

Figure 1. Molecular structure of DEA·OABA with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The intramolecular H-bond is shown by the dotted line.

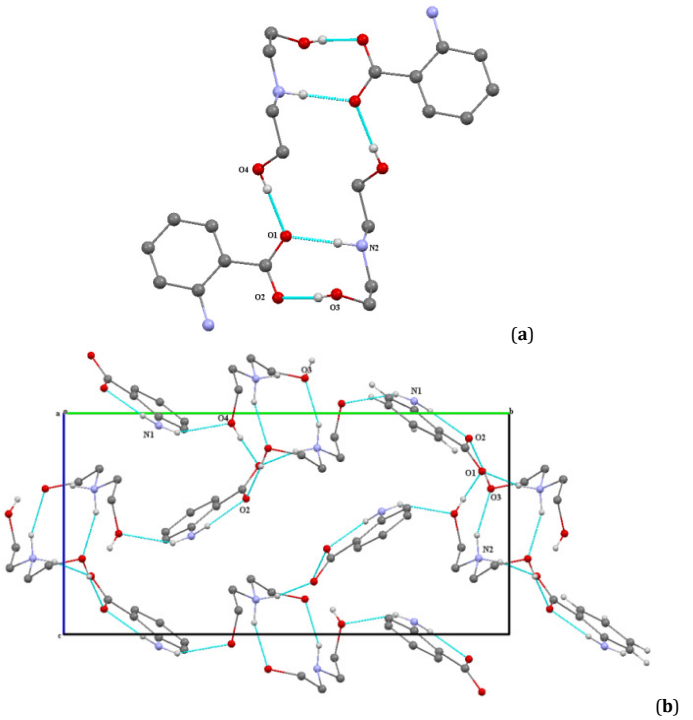

Figure 2. Supramolecular structure of DEA·OABA (H-bonds are shown as dotted lines): a) centrosymmetric tetramer $R_4^4(24)$ formed from $R_2^2(9)$ dimers. H-atoms not involved in hydrogen bonding and intramolecular H-bonds are omitted for clarity; b) packing into 3-D network of the columns generated from tetramers.

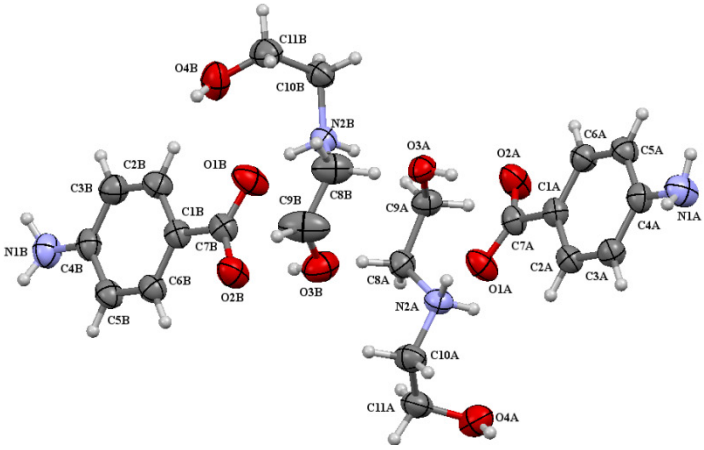

Figure 3. Molecular structure of DEA·PABA with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

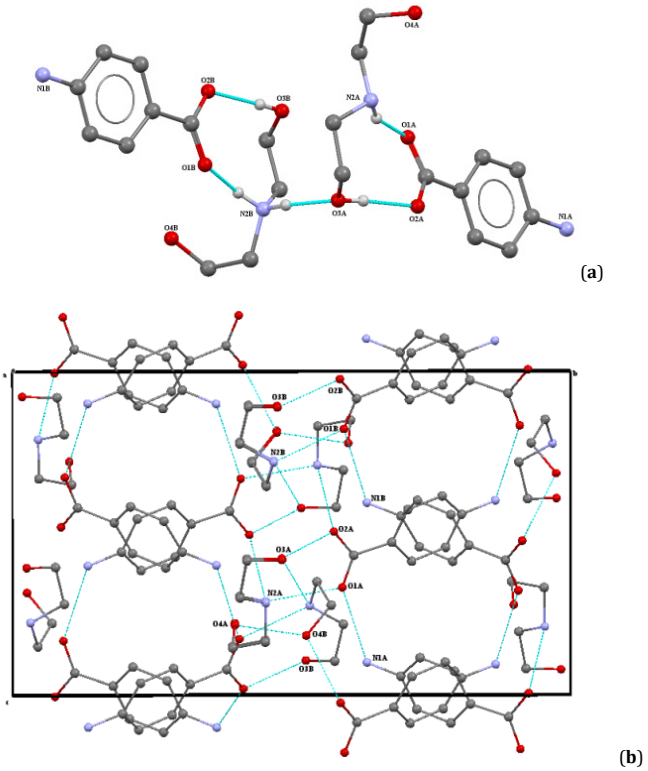

Figure 4. Crystal structure of the DEA·PABA (intermolecular H-bonds are shown as dotted lines): a) "cation-anion" dimers incorporated by the N···O H-bond. H-atoms not involved in hydrogen bonding are omitted for clarity; b) packing structure.

3.2. X-ray single crystal structure of DEA·PABA

There are two PABA and two DEA molecules (A and B) in the asymmetric part of the monoclinic unit cell (Figure 3). Acid molecules are in the benzoate form. The nitrogen atom of the DEA molecules is protonated. It is obvious that conformations of the independent molecules are different. The planes of the carboxylate groups are tilted with respect to aromatic rings at angles of 16.54 and 10.51° in molecules A and B, respectively. DEA molecules are not in extended forms because OH-groups are inclined to different values from mean line of the molecules: O···O distances are 5.911 and 4.839 Å in the molecules A and B, accordingly.

Due to existing of 12 centers capable to H-bonding an intricate system of the ten H-bonds is formed in the crystal structure. Despite of an essential difference in the molecular structure of the acidic component in respect to the previous compound the same supramolecular association between cationic and anionic units is observed: DEA molecules are H-bound to carboxylate groups of PABA molecules through the nitrogen and oxygen atoms remaining one OH-group free of H-bonding. Both independent molecules of type A and B generate identical dimers which are described by graph-sets with notations of $R_2^2(9)$. Different type dimers are associated by N2B-H···O3A bond (Figure 4a) into tetramers. Further these tetramers are associated by N2A-H2AB···O2A bond which is enhanced through a participation of the two additional H-bonds of the O4B atom O4B-H···O2B and O4B···H-O4B (Figure 4b). These H-bonds form centrosymmetric cycles with different sizes the maximal dimension ring of which is $R_2^4(20)$-graph-set cycle. The relatively weak H-bonds of the amino

groups (Table 2) incorporate structural units in direction of the *b*-axis into 3D-network structure.

Thus, all 12 atoms capable to H-bonding participate in H-bonds giving rise to the 3D-network structure. Carboxylate group oxygen atoms demonstrate double acceptor properties while OABA nitrogen atoms-double donor potencies. Hydroxyl oxygen atoms O3A and O4B show donor and acceptor capabilities.

3.3. CSD survey

DEA, OABA and PABA are well-known and easily available compounds. A lot of research work has been performed on these compounds studying their coordination and supramolecular complex formation properties. Therefore, a survey of the data reported in Cambridge Structural database (CSD) is desirable.

In CSD 11 organic salts of DEA (GIFTEU, ITHFOR, MIFRUQ, etc.) are documented. It is evident that in all these compounds an N-atom of the DEA molecule is protonated and counter ions are anions of acids except of the two phenols (QECHOX, NINZAN) and one base (OHUWIZ). The only relevant CSD entry is the compound with refcode LIXBAG which is salt between DEA and *p*-nitrobenzoic acid [20]. The same supramolecular association of the cationic and anionic components into dimers found in our title compounds is observed in this compound.

Molecules of OABA and PABA contain COOH- and NH_2-groups which make them apt to yield salts with acids or bases. Indeed, in the CSD 12 salts of OABA with acids (HOFZEI, YIKCOM, BEXQEB, etc.) and 5 entries with organic bases (ALORAV, MEDBEE, SECXOP, VAPLIH and YAGPUT) are documented. In contrast, there are 32 salts of PABA with bases (VUKPIC, XADGOY and BUHNOJ, etc.) and 23 hits with acids (WEPTUH, ZEGFEY and FLFBEU, etc.) in the database. In 4 cases (PAZKOS, UPULEX, VOJLIQ and YACNOF) PABA molecules are found in the inner salt (zwitterion) form.

No salts of OABA and PABA with ethanolamines are reported in the CSD.

4. Conclusion

DEA prefers to be crystallized with OABA and PABA in the form of salts under our preparation conditions. In both salts cations are associated with anions into dimers by the same H-bonding which closes cycles with the graph-set notations of $R_2^2(9)$. The analogical 1:1 association mode is found in salts of DEA with *p*-nitrobenzoic [20] and *o*-nitrobenzoic acid [21].
Thus, H-bonding which generates these dimers may be considered as a synthon responsible for yielding of salts between DEA and mono-substituted benzoic acids.

Supporting information

CCDCs 1477695 and 1477696 contain the supplementary crystallographic data for DEA·OABA and DEA·PABA. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Disclosure statement

Conflict of interests: The authors declare that they have no conflict of interest.
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