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Molecular recognition of acyclic amines I: co-crystallization of 2,2'-(ethylenedioxy)-diethylamine with dicarboxylic acids

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X-Ray structures of three co-crystals of 2,2'-(ethylenedioxy)-diethylamine, normally occuring in liquid phase, with two molecules of fumaric - 1a, maleic - 1b, and one molecule of adipic acid - 1d, have been determined. Two conformations of the diamine molecule with different degrees of folding have been found in the crystal. Very selective molecular recognition between diprotonated diamine 1 and dicarboxylic acid molecules was observed in three crystal structures. Aggregates being building blocks of the co-crystals included one doubly protonated diamine molecule and six diacid molecules at different protonation levels, hydrogen-bonded through carbonyl groups.

INTRODUCTION

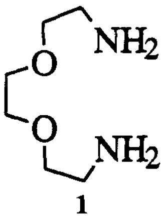
Acyclic amines containing ether functions, and their hydrochlorides, are common substrates in the synthesis of macrocyclic crown ethers containing nitrogen functions[1–4]. Formation of a macrocyclic ring from linear substrates requires some conformational changes which would favour ring closure instead of polymeric chain propagation. Yields and stereochemistry of such a reaction are strongly dependent on the conformation and molecular recognition properties of the substrates and solvents used during the reaction[1,5]. Therefore, rational control of molecular aggregation of substrates seems to be one of the most challenging problems of modern chemistry. In order to develop strategies for such an approach, a knowledge of molecular recognition between different types of compounds, which is coded by molecular formula, is indispensable.

Solid state studies of molecular conformations usually show several low energy conformations, with the geometry affected by numerous noncovalent interactions which are, in part, the crystal lattice forces. Detailed analysis of intermolecular interactions in the crystal is an especially valuable method for identification of types and the evaluation of the energy of the most frequently observed patterns of interactions (as detailed examples see ref. 6–10). This is possible due to the extensive use of recent versions of the Cambridge Crystallographic Data Base[11].

At present, no solid state structural information about 2,2'-(ethylenedioxy)-diethylamine **1** and its derivatives is found in the Cambridge Crystallographic Data Base, mostly because the compounds occur in the liquid phase. Therefore, we applied the co-crystallization technique in order to “solidify” the title compound and to observe its conformation in different crystal cavities. This paper presents the preparation of several co-crystals of **1** with dicarboxylic acids, and discusses the crystal and molecular structure of three co-crystals with maleic **1a**, fumaric **1b**, and adipic **1d** acid.

MATERIALS AND METHODS

2,2'-(ethylenedioxy)-diethylamine **1**, maleic, fumaric, adipic, succinic, and picric acids were purchased from Sigma. (+)-Camphoro-10-sulfonic acid was purchased from Fluka. All of these were used without purification.



1

1a - maleic acid
1b - fumaric acid
1c - succinic acid
1d - adipic acid
1e - picric acid
1f - (+)camphorosulfonic acid

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TABLE 1. Types, molecular ratio, and melting points of co-crystals of the 2,2'-(ethylenedioxy)-diethylamine **1** with dicarboxylic acids.

Compound	acid	amine:acid	m.p.(°)
1a	maleic acid	1:2	110–112
1b	fumaric acid	1:2	175–178
1c	succinic acid	1:2	158–160
1d	adipic acid	1:1	140–142
1e	(+)camphoro-10-sulfonic acid	1:2	164–166

Preparation of co-crystals

Different compounds containing carbonyl groups (which are usually present in the second substrate used in a macrocyclization reaction) were tested for the ability to form co-crystals with high, stable melting points. Finally, dicarboxylic acids have been chosen for further studies because they provided symmetrical couterparts for the diamine molecule.

Table 1 shows the types of compounds prepared, with the molcular ratio (known from elemental analysis), and melting points. The procedure involved the mixing of 1 mmole of diamine **1** with 1 mmole of diacid, each dissolved in 20 mL of MeOH. When possible, the crystals were removed from solution as soon as they formed, and before the solvent completely evaporated. Alternately, co-crystals with fumaric acid were prepared

TABLE 2. Crystal data and measurement conditions

	1a	**1b**	**1d**
General formula	$C_{14}H_{24}N_2O_{10}$	$C_{14}H_{24}N_2O_{10}$	$C_{12}H_{26}N_2O_6$
Molecular weight (M_r)	380.35	380.35	294.34
Crystal system	orthorhombic	monoclinic	triclinic
Space group	Pbca	$P2_1/a$	P(−1)
Z	4	4	1
Cell constants: a (Å)	9.294(2)	9.332(1)	5.4091(8)
b (Å)	16.115(3)	16.470(2)	6.8240(9)
c (Å)	12.074(2)	12.2977(8)	11.333(1)
α (°)			100.95(1)
β (°)		110.56(1)	99.23(1)
γ (°)			99.88(1)
Cell volume (Å^3)	1808.4(6)	1769.8(3)	396.48(9)
Number of electrons F(000)	808	808	160
Calculated density (g cm^{-1})	1.397	1.427	1.232
Linear absorption co-eff. $\mu(CuK_\alpha)$ (cm^{-1})	9.86	10.07	7.86
Radiation		Cu K_α (1.54178 Å)	
Number of reflections, measured;	4067	4014	1752
unique of $I > 2\sigma_I$ (R_{int})	1772 (0.04)	2827 (0.03)	1541(0)
Scan mode		θ/2θ	
Scan range ($2\theta_{max}$) (°)		150	
h, k, l_{range}	11, 20, 15	11, 20, 15	6, 8, 14
R	0.040	0.046	0.058
R ($w = 1/\sigma^2_F$)	0.049	0.043	0.062
$\Delta\rho_{max}$ (e/Å^3)	0.20	0.21	0.38
$\Delta\rho_{min}$ (e/Å^3)	−0.18	−0.24	−0.30

TABLE 3. Atomic fractional coordinates (×10^4) and *B*-equivalent[a] temperature factors for non-hydrogen atoms

	1a				**1b**				**1d**			
	x/a	*y/b*	*z/c*	B_{eq}	*x/a*	*y/b*	*z/c*	B_{eq}	*x/a*	*y/b*	*z/c*	B_{eq}
O(1)	5432(1)	2923(1)	2085(1)	3.86(3)	3301(2)	6857(1)	3210(1)	3.09(6)	3992(2)	4787(1)	6768(1)	3.32(3)
O(2)	6934(1)	3964(1)	2253(1)	4.39(4)	5532(2)	6477(1)	4492(1)	3.06(6)	4923(2)	1738(1)	6388(1)	3.27(3)
C(1)	5742(1)	3666(1)	1957(1)	3.03(3)	4167(2)	6675(1)	4225(2)	2.23(7)	4705(2)	3315(2)	7109(1)	2.45(3)
C(2)	4637(1)	4217(1)	1445(1)	3.19(3)	3469(2)	6705(1)	5150(2)	2.27(7)	5411(3)	3357(2)	8472(1)	2.93(4)
C(3)	—	—	—	—	—	—	—	—	4546(3)	4982(2)	9326(1)	2.79(4)
C(4)	4633(2)	5034(1)	1284(1)	3.44(4)	1992(2)	6712(1)	4922(2)	2.24(7)	Atoms O(1) through C(3) inverted with respect to 1/2 ,1/2,1			
C(5)	5736(2)	5678(1)	1538(1)	3.64(3)	1264(2)	6734(1)	5833(2)	2.17(7)				
O(3)	6946(1)	5460(1)	1979(1)	4.40(4)	−92(2)	6499(1)	5544(1)	2.91(6)				
O(4)	5469(2)	6401(1)	1329(1)	5.18(4)	2068(2)	6992(1)	6822(1)	2.82(6)				
O(1')	—	—	—	—	879(2)	7134(1)	8362(1)	3.04(6)	—	—	—	—
O(2')	—	—	—	—	1536(2)	8441(1)	8452(1)	3.52(7)	—	—	—	—
C(1')	—	—	—	—	1035(2)	7862(1)	8812(2)	2.48(7)	—	—	—	—
C(2')	—	—	—	—	553(2)	7935(1)	9841(2)	2.50(7)	—	—	—	—
C(4')	—	—	—	—	36(3)	7324(1)	10277(2)	2.76(8)	—	—	—	—
C(5')	—	—	—	—	−472(3)	7367(1)	11299(2)	2.64(7)	—	—	—	—
O(3')	—	—	—	—	−838(2)	6760(1)	11686(1)	3.56(7)	—	—	—	—
O(4')	—	—	—	—	−480(2)	8094(1)	11710(1)	3.19(7)	—	—	—	—
N(1)	2725(1)	2094(1)	1782(1)	3.15(3)	2748(2)	8787(1)	6640(2)	2.74(6)	3483(2)	1912(2)	4009(1)	2.64(3)
C(7)	2626(2)	2140(1)	555(1)	3.40(3)	2682(3)	9678(1)	6752(2)	3.20(7)	686(3)	1769(2)	3771(1)	3.47(4)
C(8)	3894(2)	1730(1)	15(1)	3.78(4)	3758(3)	9969(2)	7894(2)	3.42(7)	−291(3)	2068(3)	2510(1)	3.42(4)
O(7)	3877(1)	878(1)	303(1)	3.85(3)	5266(2)	9778(1)	7955(1)	3.15(5)	417(2)	593(1)	1636(1)	3.03(3)
C(9)	5049(2)	443(1)	−169(2)	4.38(5)	6338(3)	9846(2)	9109(2)	3.19(7)	−510(3)	747(2)	424(1)	2.92(4)
C(10)	Atoms N(1) through C(9) inverted with respect to 1/2,0,0				7909(3)	9621(2)	9141(2)	3.53(7)	Atoms N(1) through C(9) inverted with respect to 0,0,0			
O(10)					8602(2)	10253(1)	8695(1)	3.33(5)				
C(11)					8821(3)	10081(2)	7640(2)	3.67(8)				
C(12)					7482(3)	10347(1)	6615(2)	3.32(7)				
N(2)					7230(3)	11233(1)	6649(2)	3.01(6)				

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[a] Calculated from anisotropic thermal parameters as $B_{eq} = 8\pi^2 \cdot U_d^{1/3}$ where U_d is the determinant of the *U* matrix (in orthogonal space for **1b** and **1d**).

TABLE 4. Bond lengths (Å)

	1a	**1b**	**1d**		**1a**	**1b**	**1d**
C(1)-O(1)	1.241(2)	1.262(2)	1.241(2)	C(5a)-C(4a)	–	1.493(4)	–
C(1)-O(2)	1.259(2)	1.242(3)	1.257(1)	O(3a)-C(5a)	–	1.207(3)	–
C(2)-C(1)	1.492(2)	1.497(4)	1.524(2)	O(4a)-C(5a)	–	1.301(2)	–
C(3)-C(2)	–	–	1.517(2)	N(1)-C(7)	1.486(2)	1.477(2)	1.476(2)
C(3')-C(3)	–	–	1.522(2)	C(7)-C(8)	1.500(2)	1.490(3)	1.506(2)
C(4)-C(2)	1.331(2)	1.307(3)	–	O(7)-C(8)	1.416(2)	1.418(3)	1.420(2)
C(5)-C(4)	1.491(2)	1.501(4)	–	C(9)-O(7)	1.415(2)	1.425(2)	1.415(2)
C(5)-O(3)	1.293(2)	1.250(3)	–	C(10)-C(9)	1.488(2)	1.499(4)	1.503(2)
C(5)-O(4)	1.218(2)	1.258(2)	–	O(10)-C(10)	–	1.432(4)	–
C(1a)-O(1a)	–	1.307(2)	–	C(11)-O(10)	–	1.411(3)	–
C(1a)-O(2a)	–	1.212(3)	–	C(12)-C(11)	–	1.495(3)	–
C(2a)-C(1a)	–	1.489(4)	–	N(2)-C(12)	–	1.481(2)	–
C(4a)-C(2a)	–	1.309(3)	–				

Atom C(3') is C(3) inverted with respect to (1/2,1/2,1); atom C(10) corresponds to C(9) inverted with respect to (1/2,0,0); atom C(10) corresponds to C(9) inverted with respect to (0,0,0).

by a solid state technique (after the 1:2 ratio was known), by grinding the substrates for 15 min in the mortar, and then finally warming up to 80°C. The prepared compund has an appropriate, stable melting point.

X-ray structure determination

Monocrystals of compounds **1a**, **1b**, and **1d** were mounted on a CAD4 diffractometer. Unit cell parameters were determined on the basis of 25 well-centered reflections. Crystal data for compounds **1a**, **1b**, and **1d** and details of measurement conditions and structure refinement are shown in Table 2. Intensities were corrected for LP and variation in the intensity of three standard reflections. The structure was solved by direct methods (SHELXS86)[12] and refined by full-matrix least squares, minimizing $\Sigma w(\Delta F)^2$, where $w = 1/\sigma^2(F)$, and sigma was obtained from counting statistics (SHELX76)[13]. All hydrogen atoms were found from ΔF synthesis and refined with isotropic displacement parameters. All calculation were performed on a PC/486 computer, using the programs quoted above and our own supporting programs. Table 3 gives atomic coordinates (10^4) for the three compounds, and Table 4 and 5, bond lengths and bond angles, respectively.

RESULTS AND DISCUSSION

Conformation of *1*

Co-crystallization of diamine **1** with dicarboxylic acid molecules resulted in proton transfer from the carboxyl to amine groups. For compounds **1a** and **1b**, where the amine-to-acid ratio is 1:2, the degree of deprotonation depends on the acid molecule configuration. Only one hydrogen atom from the maleic acid molecule was transferred in compound **1a**, whereas in the case of compound **1b**, two different molecules of fumaric acid are present in the crystal: one doubly deprotonated and the second, neutral. For compound **2d**, with amine-to-acid ratio 1:1, both protons from adipic acid were transferred to the amine nitrogens, and the crystal lattice consists of doubly ionized anions and cations. Unit cell parameters for compounds **1a** and **1b** are very close (see Table 2). The asymmetric unit of compound **1a** contains 0.5 molecule of diamine and 1 molecule of maleic acid,

TABLE 5. Valence angles (°)

	1a	**1b**	**1d**		**1a**	**1b**	**1d**
O(1)-C(1)-O(2)	122.5(1)	124.4(2)	123.8(1)	C(1a)-C(2a)C(4a)	–	123.4(2)	–
O(1)-C(1)-C(2)	117.8(1)	116.4(2)	120.2(1)	C(2a)-C(4a)-C(5a)	–	125.4(2)	–
O(2)-C(1)-C(2)	119.8(1)	119.2(2)	115.9(1)	C(4a)-C(5a)-O(3a)	–	120.7(2)	–
C(1)-C(2)-C(3)	–	–	115.7(1)	C(4a)-C(5a)-O(4a)	–	114.7(2)	–
C(2)-C(3)-C(4)	–	–	112.9(1)	O(3a)-C(5a)-O(4a)	–	124.6(3)	–
C(1)-C(2)-C(4)	130.6(1)	123.0(2)	–	N(1)-C(7)-C(8)	111.3(1)	111.8(2)	111.7(1)
C(2)-C(4)-C(5)	131.1(2)	124.1(2)	–	C7-C(8)-O(7)	108.1(1)	107.8(2)	108.3(1)
O(3)-C(5)-C(4)	119.6(2)	117.3(2)	–	C(8)-O(7)-C(9)	111.9(1)	111.8(2)	111.3(1)
O(4)-C(5)-C(4)	118.9(2)	117.2(2)	–	O(7)-C(9)-C(10)	108.5(2)	110.2(2)	107.4(1)
O(3)-C(5)-O(4)	121.5(2)	125.5(2)	–	C(9)-C(10)-O(10)	–	112.3(2)	–
O(1a)-C(1a)-O(2a)	–	124.5(2)	–	C(10)-O(10)-C(11)	–	115.9(2)	–
O(1a)-C(1a)-C(2a)	–	114.3(2)	–	O(10)-C(11)-C(12)	–	111.6(2)	–
O(2a)-C(1a)-C(2a)	–	121.1(2)	–	C(11)-C(12)-N(2)	–	111.0(2)	–

Atom C(4) generated by inversion of C(3) at (1/2,1/2,1); atom C(10) generated by inversion of C(9) at (1/2,0,0); atom C(10) generated by inversion of C(9) at (0,0,0).

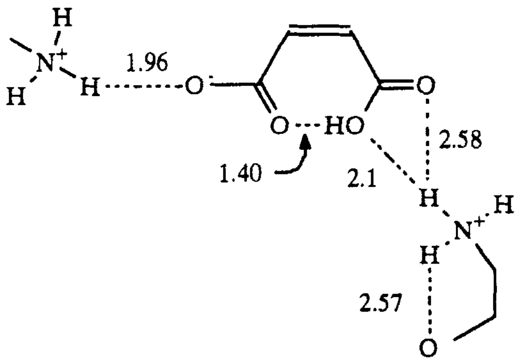
TABLE 6. Torsion angles (°) in the diamine molecule[a]

	1a	1b	1d
O(7)-C(8)-C(7)-N(1)	62.8(2)	62.9(3)	57.0(2)
C(9)-O(7)-C(8)-C(7)	−179.6(1)	−165.4(2)	178.2(1)
C(10)-C(9)-O(7)-C(8)	−179.9(2)[b]	178.7(2)	175.5(1)[b]
O(10)-C(10)-C(9)-O(7)	180[b]	76.6(3)	180[b]
C(11)-O(10)-C(10)-C(9)		−112.3(2)	
C(12)-C(11)-O(10)-C(10)		91.3(3)	
N(2)-C(12)-C(11)-O(10)		60.2(3)	

[a] The angles for symmetric parts of the molecules are omitted. [b] Atoms C(10) and O(10) are generated from C(9) and O(7), respectively, by inversion at (1/2,0,0) for 1a, and at (0,0,0) for 1d.

whereas in the case of compound **1b** it contains one molecule of amine and two molecules of fumaric acid. The asymmetric unit of compound **1d** contains one half of each molecule. This shows that two-fold local symmetry of the amine molecule can be maintained in the crystal.

The conformation of the diamine molecule in the crystal is of importance. It is usually drawn in the folded form on schemes describing reaction pathways. Intuitively, it should have this conformation in solution during stages preceeding the reaction involving ring closure. In the present case, the conformation of the amine molecule observed in co-crystals with maleic and adipic acid is very similar, and is characterized by two terminal torsion angles close to 60° (see Table 6). The remaining seven torsion angles are close to ±180°. When diamine **1** co-crystallizes with fumaric acid the conformation of the amine is, as it is shown in Fig. 1, unsymmetrically folded. Interestingly, none of the above conformations is affected by intramolecular hydrogen bonds of classic geometry (i.e. acceptor...H distance below 2.4 Å), formed between amine hydrogen and chain oxygen atoms. Only in the case of compound **1d** was a quite long distance found: 2.58 Å between ring oxygen O7 and proton H10. The reason for this geometry might be the fact that the same proton takes part in two other intermolecular interactions with O3 and O4 atoms from neighbouring carboxyl groups (see Table 7).



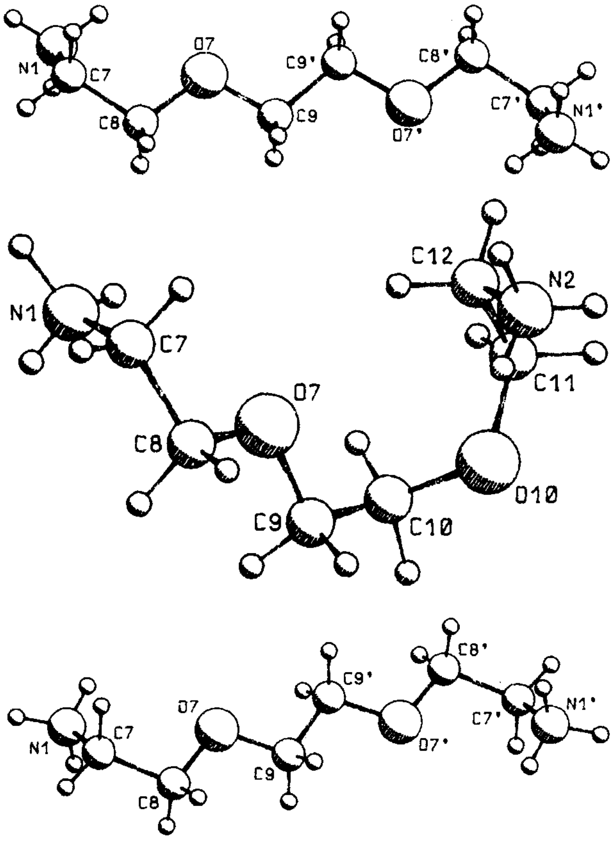


Figure 1. Diagrams of the quaternized amine molecules of **1a**, **1b**, and **1d** oriented arbitrarily to show an optimal view.

Amine—acid interactions

As it was expected, molecular recognition between the two species is due to an extensive system of intermolecular hydrogen bonds. As is seen from Table 7, each ammonium group forms three hydrogen bonds with oxygen atoms from carboxyl groups belonging to different dicarboxylic acid molecules. The simplest systems for the above interactions are shown in Figures 2,3 and 4, for compounds **1a**, **1b**, and **1d**, respectively. It is also a

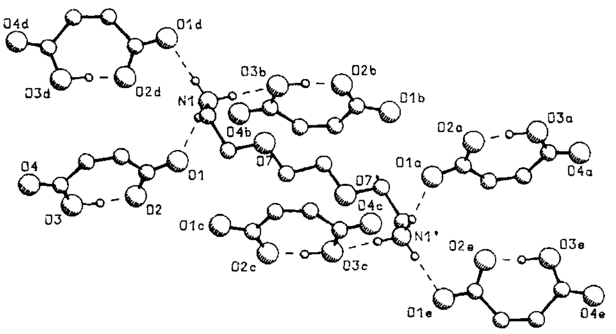


Figure 2. A simplified hydrogen-bonding system in **1a**: the amine molecule is surrounded by six maleic acid molecules. Carbon labels and C-attached hydrogen atoms are omitted for clarity.

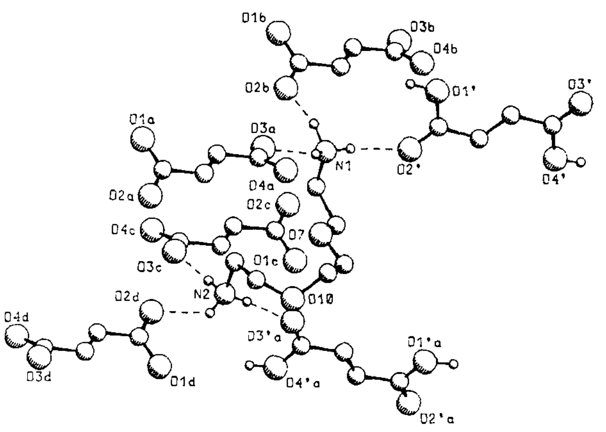


Figure 3. A simplified hydrogen-bonding system in **1b**: the amine molecule is surrounded by six fumaric acid molecules. Carbon labels and C-attached hydrogen atoms are omitted for clarity.

characteristic of this recognition pattern that amine molecules containing oxygen atoms competing for amine protons, do not completely interact mutually, and aggregates consisting of one di-protonated amine molecule and six acid molecules are building blocks of the crystal lattice. The affinity of ammonium ion protons to carbonyl oxygen atoms is very selective and does not depend on the protonation level of the carboxyl group. From the distances between donor and acceptor molecules shown in Table 7, one can see that hydrogen bonds observed in the crystal of compound **1d**, consisting of doubly ionized cations and anions, are stronger when compared to the analogous set of hydrogen bonds in compounds **1a** and **1b**.

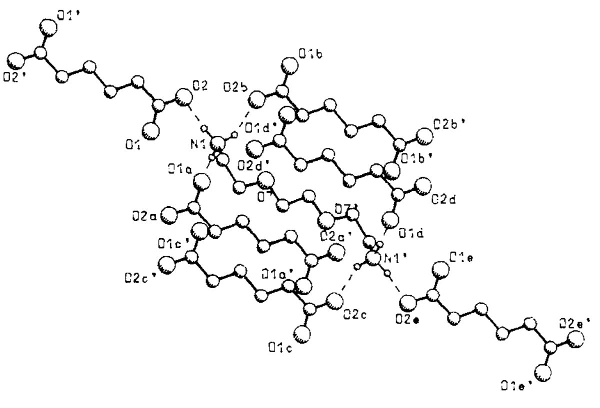


Figure 4. A simplified hydrogen-bonding system in **1d**: the amine molecule is surrounded by six adipic acid molecules. Carbon labels and C-attached hydrogen atoms are omitted for clarity.

Acid—acid interactions

It was found some time ago that dicarboxylic acids like fumaric, succinic, adipic, etc., form in the solid state dimers which are expanded in the crystal lattice into ribbons[14]. It was of interest to see if some structural elements of this pattern could be retained in the above co-crystals, especially in the case when acid molecules occupy two-thirds of the unit cell volume. In the present case, the number of protons transferred from the acid molecule to the amine group varies, depending on the configuration of the acid molecule, and on the amine-to-acid ratio. In compound **1a**, containing maleic acid with carboxyl groups in the Z configuration, one proton from each acid molecule was transferred to the amine, and the second formed a strong intramolecular hydrogen bond. A

TABLE 7. Geometry of hydrogen bond interactions*

Compound 1a				
Hydrogen bridge (acceptor symmetry)	D...A(Å)	D–H(Å)	H...A(Å)	D–H...A(°)
1) N1 - H9 ... O1 (x,y,z)	2.872	0.94	1.96	164
2) N1 - H10 ... O7 (x,y,z)	2.859	0.97	2.57	97
3) N1 - H10 ... O3 (1 − x,y − 1/2,1/2 − z)	3.044	0.97	2.11	163
4) N1 - H10 ... O4 (1 − x,−y − 1/2,1/2 − z)	3.044	0.97	2.58	110
5) N1 - H11 ... O1 (x − 1/2,y,1/2 − z)	2.863	0.90	1.96	177
6) O3 - H12 ... O2 (x,y,z)	2.433	1.05	1.40	168
Compound 1b				
Hydrogen bridge (acceptor symmetry)	D...A(Å)	D–H(Å)	H...A(Å)	D–H...A(°)
1) N1 - H17 ... O3 (1/2 + x,3/2 − y,z − 1)	2.830	0.93	2.05	142
2) N1 - H18 ... O2A (x,y,z)	2.888	0.84	2.11	156
3) N1 - H19 ... O2 (x − 1/2,3/2 − y,z)	2.758	1.07	1.70	167
4) N2 - H20 ... O3A (1/2 − x,1/2 + y,2 − z)	2.916	0.84	2.09	166
5) N2 - H21 ... O3 (1/2 − x,1/2 + y,1 − z)	2.769	1.06	1.74	163
6) N2 - H22 ... O2 (3/2 − x,1/2 + y,1 − z)	2.924	0.88	2.26	133
7) N2 - H22 ... O4A (1 − x,2 − y,2 − z)	3.194	0.88	2.53	133
8) O1A - H23 ... O4 (x,y,z)	2.520	1.00	1.53	174
9) O4A - H24 ... O1 (x − 1/2,3/2 − y,1 + z)	2.485	0.95	1.54	178
Compound 1d				
Hydrogen bridge (acceptor symmetry)	D...A(Å)	D–H(Å)	H...A(Å)	D–H...A(°)
1) N1 - H11 ... O2 (1 − x,−y,1 − z)	2.754	0.89	1.95	149
2) N1 - H12 ... O1 (1 − x,1 − y,1 − z)	2.793	0.97	1.82	176
3) N1 - H13 ... O1 (x,y,z)	3.303	0.97	2.59	130
4) N1 - H13 ... O2 (x,y,z)	2.715	0.97	1.75	172

*Estimated standard deviations for compounds:
1a: N...O 0.002 Å; N-H 0.02 Å; H...O 0.02 Å; angle 0.5°
1b: N...O 0.002 Å; N-H 0.02 Å; H...O 0.02–0.03 Å; angle 0.06–0.07°
1d: N...O 0.002; N-H 0.02 Å; H...O 0.02 Å; angle 0.06–0.07°

similar geometry of hydrogen bonds was found in the maleic acid structure[15–17].

No other acid-acid interactions were found in the crystal lattice, as in the case of the crystal lattice of compound **1d**, where the amine-to-acid ratio is 1:1, and no protons are available for intermolecular interactions. In the structure of **1b**, one of the two independent fumaric acid molecules is doubly deprotonated, and the second has both protons available. They form ribbons of singly-bonded acid molecules.

CONCLUSIONS

The use of hydrogen bonding interactions has been demonstrated for obtaining structural information about 2,2'-(ethylenedioxy)-diethylamine **1**, normally a liquid. Very selective molecular recognition between diamine **1** and dicarboxylic acid molecules was observed in three crystal structures. Host-guest aggregates included six diacid molecules, hydrogen-bonded to two ammonium ions of the amine molecule, regardless of the ratio of both molecules in the crystal, the acid molecule configuration, and the chain length. The conformation of the diamine molecule found in the crystals was affected by this aggregation behaviour. Two terminal clusters of acid molecules hydrogen-bonded to the amine molecule are found in the E configuration, and therefore, the amine molecule has both ends wrapped in opposite directions.

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