Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Materials

Toward a new type of proton conductors based on imidazole and aromatic acids

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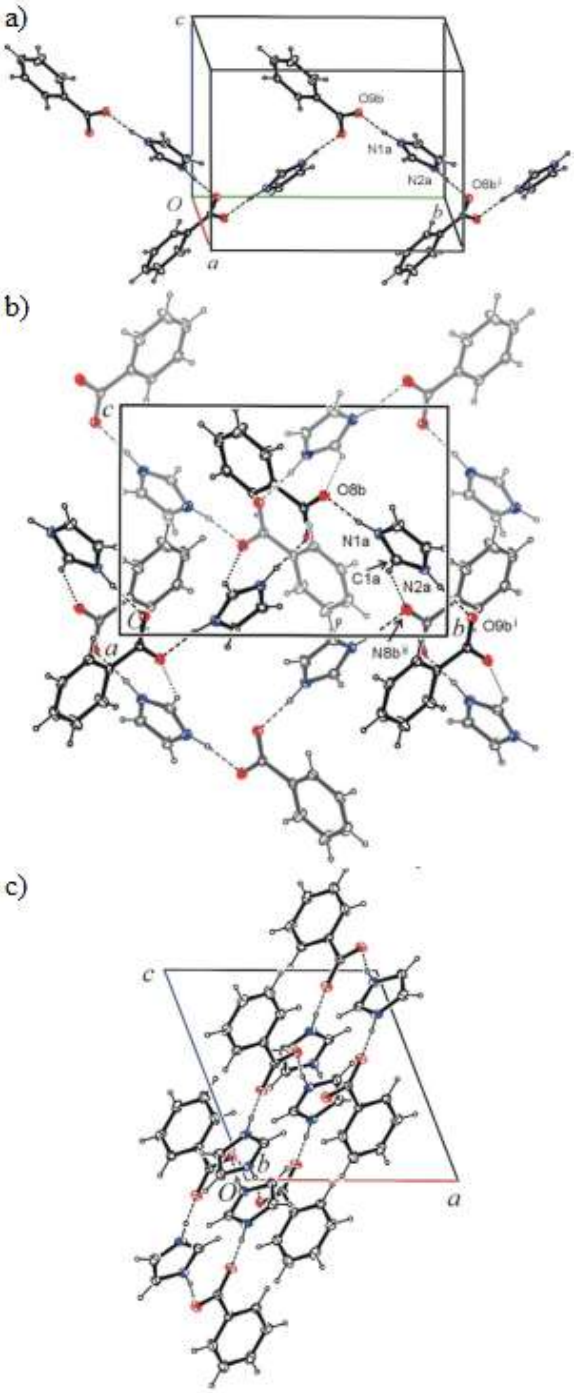

Figure S1. Part of the molecular packing of **1** in two views, showing the hydrogen-bonded (a) chain of molecules growing parallel to the *b* axis, (b,c) sheet of molecules parallel to the (-101) plane. The symmetry codes are explained in **Table 1S**.

Table S1. The geometrical parameters of D-H···A interactions for salt **1** (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1a—H1ab···O9b	0.94(2)	1.67(2)	2.6033(14)	168.4(16)
N2a—H2a···O8b^{i}	0.922(18)	1.730(18)	2.6495(14)	174.6(18)
C1a—H1aa···O9b^{ii}	0.95	2.38	3.2032(17)	145
C2a—H2aa··π(Ph^{iii})	0.95	2.66	3.5531(16)	156

Symmetry codes: (i) 1/2-*x*,1/2+*y*,1/2-*z*; (ii) -1/2+*x*,3/2-*y*,-1/2+*z*; (iii) 1/2+*x*,3/2-*y*,-1/2+*z*

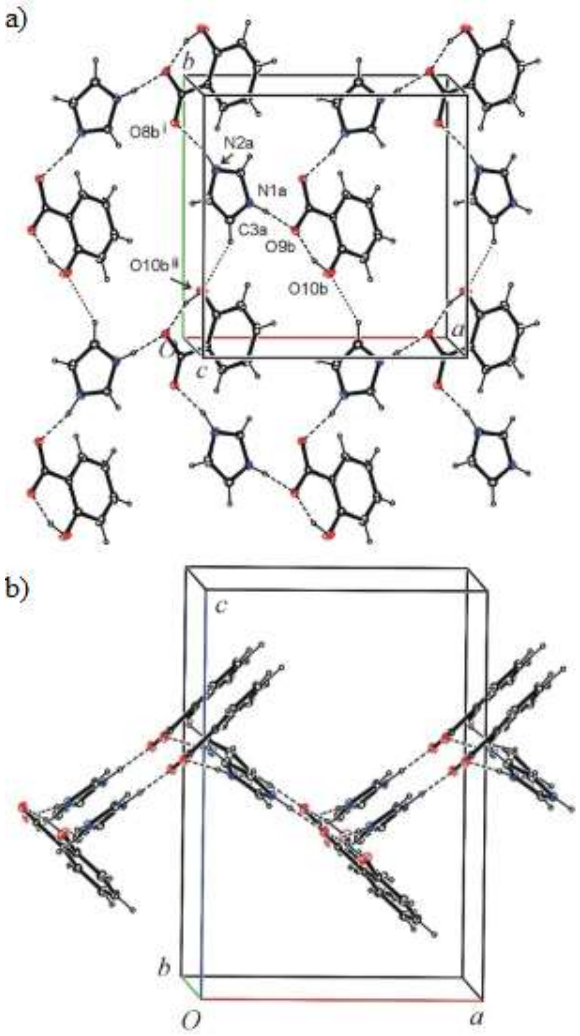

Figure S2. Two views of the unit cell of 2 showing the hydrogen-bonded sheet of molecules parallel to the *ab* plane. The symmetry codes are explained in **Table 2S**.

Table S2. The geometrical parameters of D-H···A interactions for salt **2** (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O10b—H10b···O9b	0.96(2)	1.62(2)	2.5285(14)	156(2)
N1a—H1a···O9b	0.93(2)	1.77(2)	2.6950(15)	173(2)
N2a—H2a···O8b^{i}	0.93(2)	1.77(2)	2.6798(15)	166(2)
C3a—H3aa··O10b^{ii}	0.95	2.42	3.2537(18)	147
C3a—H3aa···πPh^{iii})	0.95	2.69	3.5777(16)	156

Symmetry codes: (i) –1/2+*x*,3/2–*y*,1–*z*; (ii) –1/2+*x*,1/2–*y*,1–*z*; (iii)1/2–*x*,1– *y*,1/2+*z*

a) ***b)***

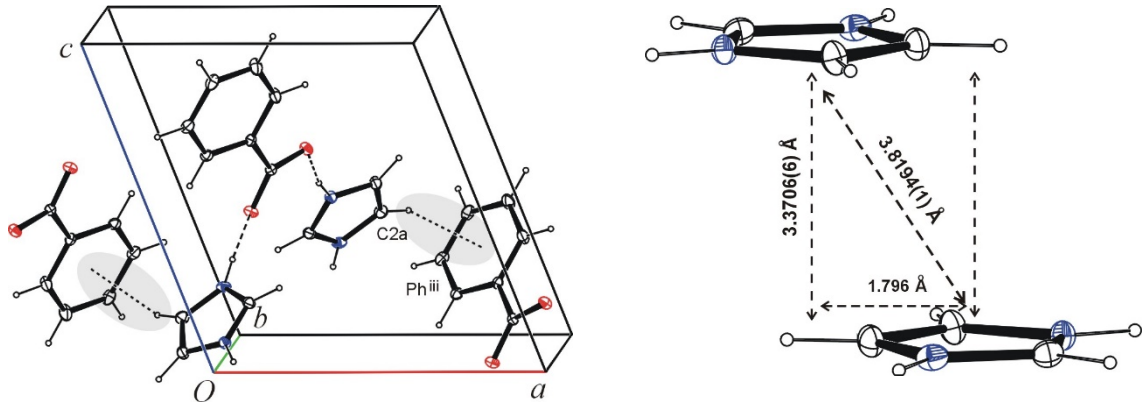

Figure S3. Intermolecular contacts: C2a-H2aa…π(Ph^{iii}) (a) and π(Im)···π(Im^{iv}) (b); symmetry codes (iii) 1/2+x, 3/2-y, -1/2+z; (iv) 1-x,2-y,1-z; Ph and Im = phenyl and imidazolium rings.

a) ***b)***

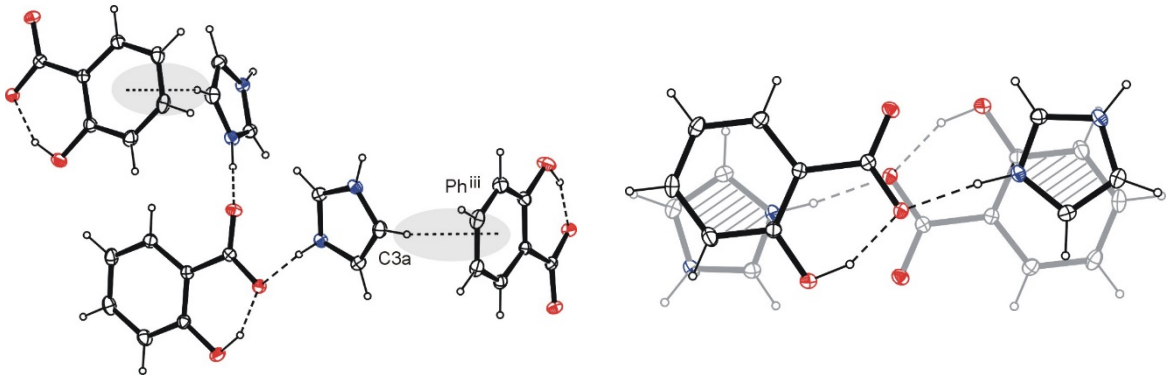

Figure S4. Intermolecular contacts of type C-H…π(Ph) (a) and of typeπ···π (b).

Table S3. NMR data interpretation. Note: The numbering of carbon and nitrogen atoms of imidazole and acids molecules are given in **Figure S5**.

	Imidazole	**Benzoic acid**	Salt **1**		**Salicylic acid**	Salt **2**
				C3b (d)	6.95	6.78
C2a, C3a	7.02		7.09	**C2a, C3a**		7.55
C3b, C5b		7.49	7.47	**C4b (t)**	7.51	7.85
C4b		7.61	7.81	**C5b (t)**	6.93	6.76
C1a	7.66		7.58			8.82
C2b, C6b		7.95	7.95	**C6b (d)**	7.79	7.30
N1a, N2a	12.1		10.98			14.01
COOH		12.95		**COOH**	13.30	14.01
				OH	11.46	
				C3b	117.11	116.37
				C5b	119.20	117.66
				C1b	112.92	118.16
C2a, C3a	135.2		135.18	**C2a, C3a**		134.62
C3b, C5b		128.58	128.50	**C6b**	130.29	130.39
C2b, C6b		129.29	129.3			
C4b		132.87	132.57			
C1b		130.79	131.6			
C1a	121.8		121.52			119.88
				C4b	135.68	133.06
C7b		167.35	167.76	**C2b**	161.17	161.90
				C7b	171.97	173.50

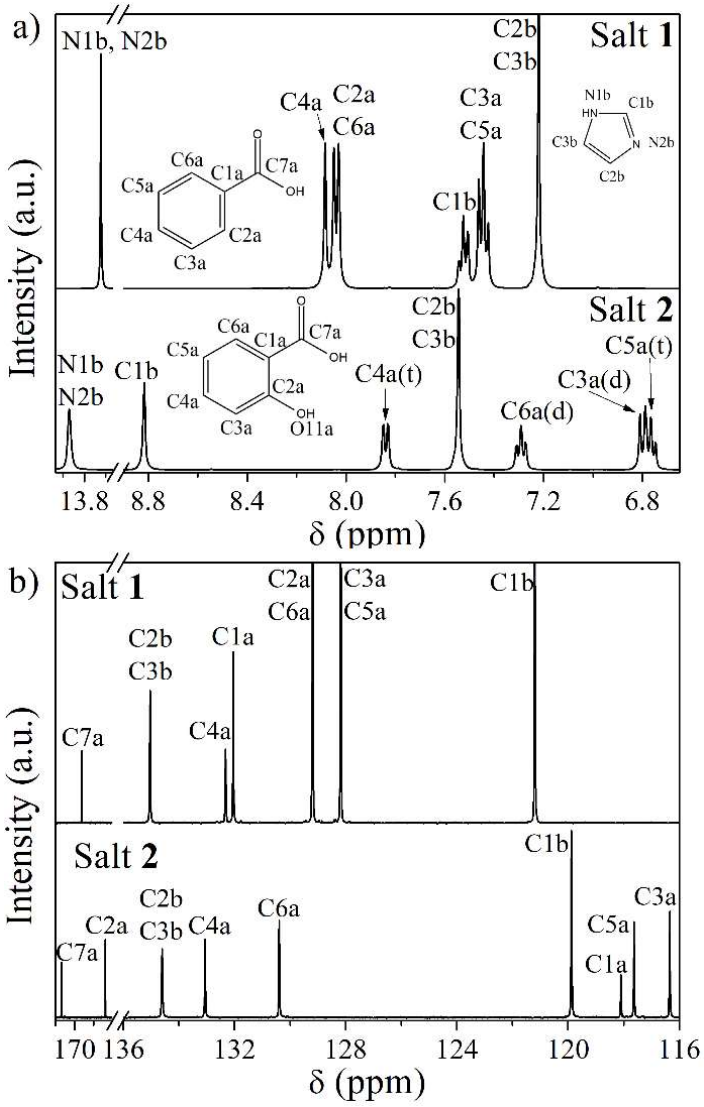

Figure S5. ^{1}H NMR (a) and ^{13}C NMR (b) solution (DMSO-d6) spectra of salt **1** and **2.**

Table S4. The geometrical parameters: bond length [Å] and bond angles [˚] of imidazolium ion of salt **1** and **2**.

	Salt **1**	Salt **2**
Bond Lengths		
N1–C1	1.325	1.323
N2–C1	1.327	1.327
N1–C3	1.368	1.366
N2–C2	1.366	1.361
C2–C3	1.349	1.340
Bond Angles		
N1-C1-N2	108.9	108.4
C1-N1-C3	108.1	108.6
C1-N2-C2	108.6	108.5
N1-C3-C2	107.6	107.1
N2-C2-C3	106.8	107.4

[b]Angles and bond lengths are defined in Fig. 1.

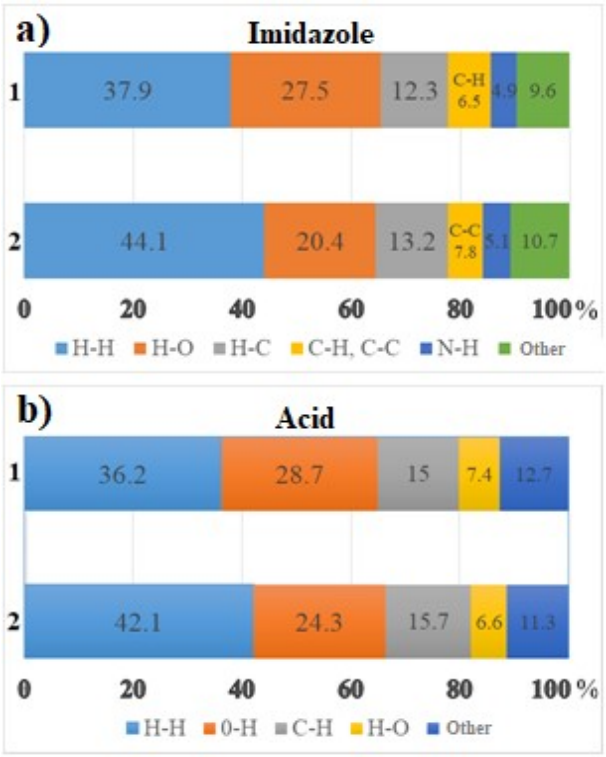

Figure S6. Close contact of imidazolium benzoate salt (**1**), imidazolium salicylate (**2**); Hirshfeld surface calculated for imidazole molecules (a) and acid molecules (b). The notation A-B refers to the interaction between A atoms inside the Hirshfeld surface and B atoms outside.

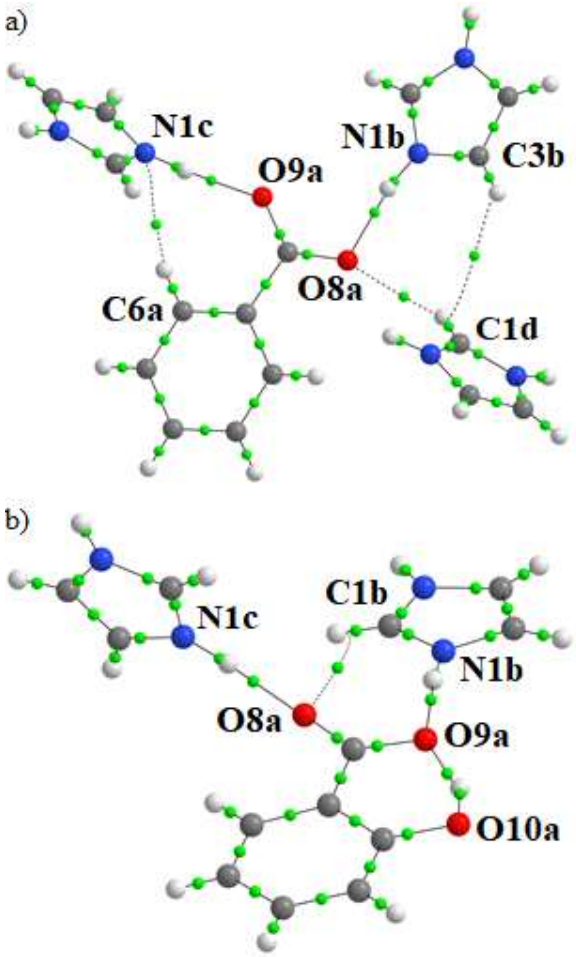

Figure S7. Molecular graphs (QTAIM) of salt **1** (a) and salt **2** (b) bound through hydrogen bonds. Green circles correspond to bond critical points (BCP).

Table S5. Geometrical parameters of D–H···A hydrogen bonds (in Å and °) and QTAIM parameters (in atomic units) corresponding to the bond critical point (BCP).

	D–H···A	$d_{H\cdots A}$ [Å]	<D-H···A [°]	D_{D-H} [Å]	$D_{D\cdots A}$ [Å]	ρ_{BCP} [a.u.]	$\Delta\rho_{BCP}$ [a.u.]	G_{BCP} [a.u.]	V_{BCP} [a.u.]	H_{BCP} [a.u.]
1	C6b–H···N1c	2.802	131.9	0.950	3.509	0.0057	0.0220	0.0044	-0.0033	0.00111
	N1c–H···O9b	1.729	174.6	0.922	2.649	0.0333	0.2121	0.0527	-0.0524	0.00033
	C1d–H···O8b	2.380	144.7	0.950	3.203	0.0096	0.0447	0.0102	-0.0091	0.00102
	N1a–H···O8b	1.671	168.4	0.944	2.603	0.0378	0.2564	0.0638	-0.0635	0.00029
	C1d–H···H	2.751	109.1	0.950	3.190	0.0019	0.0075	0.0012	-0.0006	0.00065
2	N1c–H···O8b	1.766	166.1	0.932	2.679	0.0363	0.1476	0.0362	-0.0356	0.00068
	O10b–H···O9b	1.624	155.5	0.959	2.528	0.0536	0.1882	0.0539	-0.0608	-0.00689
	C1a–H···O8b	2.840	110.4	0.950	3.294	0.0052	0.0234	0.0047	-0.0035	0.00116
	N1a–H···O9b	1.771	172.6	0.929	2.695	0.0372	0.1448	0.0363	-0.0363	-0.00006