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Tuning charge-assisted and weak hydrogen bonds in molecular complexes of the proton sponge DMAN by acid co-former substitution

Lucy K. Saunders,[a] Harriott Nowell,[a] Helen C. E. Spencer,[b] Lauren E. Hatcher,[b] Helena J. Shepherd,[b,c] Lynne H. Thomas,[b] Charlotte L. Jones,[b] Simon J. Teat,[d] Paul R. Raithby,[b,e] and Chick C. Wilson[b]

a Diamond Light Source, Harwell Science and Innovation Campus, Didcot OX11 0DE, UK

b Department of Chemistry, University of Bath, Bath, BA2 7AY, UK

c School of Physical Sciences, University of Kent, Canterbury, Kent, CT2 7NH, UK

d Advanced Light Source, Lawrence Berkeley National Lab, Berkeley CA 94270, USA

e Research Complex at Harwell, Harwell Science and Innovation Campus, Didcot, Oxfordshire, OX11 0DE, UK

E-mail: C. C.Wilson@bath.ac.uk

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Figure S2	Hirshfeld surfaces for DMANH$^+$ cations dimethylamino groups in molecular complexes **1** – **9** generated using CrystalExplorer. [1, 2] This surface shows a three-dimensional picture of

intermolecular close-contacts in terms of van der Waals (vdW) radii. [4] Red highlights those contacts shorter than the vdW radius, white indicates those around the vdW separation and blue is for longer contacts greater than the vdW separations. Here, red spots are larger and greater in number around the methyl groups of the $DMANH^+$ cation for **1** – **4** (ED) than **5** – **9** (EW), in agreement with interactions to these groups being shorter in general for the ED complexes. In the complexes, close contacts form most often to the protonated dimethylamino group shown by the increasing number of red spots to the protonated side of the cation.

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Table S10 The C—N *peri*-amino bond lengths (Å) and < angles (°) in the neutral DMAN[5] and in the $DMANH^+$ cations of the molecular complexes (see Scheme 1 for atom labels).

Table S1 Details of data collection, reduction and crystal structure solution and refinement.

For **1**, single crystal X-ray diffraction data were collected on beamline I19 in EH1 at the Diamond Light Source using Si (111) monochromated radiation at λ = 0.6889 Å on a Crystal Logic four-circle κ geometry diffractometer equipped with a Rigaku Saturn 724+ CCD area detector at 100 K. The sample temperature was controlled using an Oxford Cryosystems Cryostream Plus. Data collection was performed using the Rigaku CrystalClear™ software[6] whilst data processing was performed using Rigaku Oxford Diffraction CrysAlisPro software[7] version 1.171.37.28. For **2**, **4**, **5**, **8** and **9**, single crystal X-ray diffraction data were collected on beamline 11.3.1 at the Advanced Light Source, U.S.A using Si (111) monochromated radiation at λ = 0.8856 Å on a Bruker AXS D8 three-circle diffractometer equipped with a Bruker AXS PHOTON 100 CMOS detector at 100 K. The sample temperature was controlled using an Oxford Cryosystems Cryostream Plus. The data were collected and processed using Bruker AXS Apex2 software[8] with SADABS-2014/15.[9] For **3** and **6** single crystal X-ray diffraction data were collected at the University of Bath, U.K. using Mo-Kα (**3**) and Cu-Kα (**6**) radiation on a Rigaku Oxford Diffraction Xcalibur(**3**)/SuperNova(**6**) four-circle diffractometer equipped with an Agilent Atlas CCD detector at 150 K. The sample temperature was controlled using an Oxford Cryosystems Cryostream Plus. For **7**, single crystal X-ray diffraction data were collected at the Research Complex at Harwell (RCaH), U.K. using Cu-Kα radiation on a Rigaku Oxford Diffraction SuperNova four-circle diffractometer equipped with an Agilent Atlas CCD detector at 150 K. The sample temperature was controlled using an Oxford Cryosystems Cryostream 700. The data were collected and processed for **3**, **6** and **7** using Rigaku Oxford Diffraction CrysAlisPro software[7] version 1.171.37.33.

All structures were solved using SHELXS-2013[10] and refined using SHELXL-2013 or -2016/6[11] within the WinGX package.[12] All non-hydrogen atoms were refined anisotropically. In nearly all the molecular complexes, hydrogen atoms were located from Fourier difference maps and refined freely. The exception is that of **3** where all amino group hydrogen atoms were refined in calculated positions using HFIX 93 and for C13A, the methyl hydrogen atoms were refined in calculated positions using HFIX 137. In structure **7**, there is some evidence of disorder of 4-nitrobenzoic acid molecule E. Attempts to refine this disorder however resulted in an unstable refinement which did not improve residuals.

Table S2 The bond lengths of the carboxyl and carboxylate groups forming the O—H···O$^-$ CAHBs in each molecular complex.

	Carboxylate group		Carboxyl group	
Complex	dC—O$^-$ (Å)	dC=O (Å)	dC—OH (Å)	dC=O (Å)
1	1.280(2)	1.256(2)	1.338(2)	1.218(2)
2	1.294(2)	1.230(1)	1.289(1)	1.236(1)
3	H1A (C78I) 1.290(4)	1.240(4)	H1C (C71H) 1.315(4)	1.233(4)
	H1B (C64G) 1.288(4)	1.235(4)	(C64G) 1.288(4)	1.235(4)
	(C43D) 1.289(4)	1.242(5)	(C50E) 1.314(5)	1.224(5)
	(C57F) 1.300(4)	1.230(5)	(C57F) 1.300(4)	1.230(5)
4	1.279(2)	1.235(2)	1.304(2)	1.222(2)
5	1.257(2)	1.253(2)	1.323(2)	1.210(2)
			1.314(3)	1.211(3)
6	1.257(2)	1.249(2)	1.315(2)	1.211(2)
			1.318(2)	1.212(2)
7	H1A (C1F) 1.252(2)	1.252(2)	(C1G) 1.309(2)	1.215(2)
			(C1H) 1.317(2)	1.210(2)
	H1B (C1E) 1.252(2)	1.249(2)	(C5I) 1.311(2)	1.210(3)
			(C1D) 1.315(2)	1.212(2)
	H1C (C1K) 1.249(3)	1.249(2)	(C1L) 1.312(2)	1.219(2)
			(C1J) 1.316(2)	1.209(2)
8	1.275(1)	1.236(1)	1.312(1)	1.213(1)
9	1.254(1)	1.248(2)	-	-

Table S3 Parameters of the O—H···O^- CAHBs in each molecular complex.

Complex	Interaction	dO—H (Å)	dH···O^- (Å)	dO···O^- (Å)	<OHO^- (°)	Symmetry Operation	Substituent group class
1	O(4)-H(20)...O(4)	0.97(2)	1.71(3)	2.6659(17)	174(2)		ED
	*O(6)-H(30)...O(3)#1	0.99(2)	1.60(3)	2.5757(18)	169(2)	#1 x-1, y, z	
	*O(5)-H(29)...O(4)#3	0.99(2)	1.59(3)	2.5695(17)	170(2)	#3 –y+1/2, z+1/2	
2	O(2)-H(32)...O(3)	1.18(3)	1.27(3)	2.4495(11)	174(2)		ED
3	O(2)-H(90)...O(1)	1.19(4)	1.32(4)	2.482(3)	164(4)		ED
	O(12)-H(96)...O(10)	1.02(4)	1.50(4)	2.508(3)	167(4)		
	O(5)-H(95)...O(5)#2	1.239(2)	1.239(2)	2.478(4)	180.000(1)	#2 -x,-y,-z+2	
	O(8)-H(94)...O(8)#8	1.224(2)	1.224(2)	2.449(4)	180.00(18)	#8 -x,-y,-z+1	
4	O(4)-H(27)...O(2)	1.02(3)	1.47(3)	2.4797(16)	168(2)		ED
5	O(3)-H(27)...O(1)	1.04(3)	1.51(3)	2.5404(18)	167(3)		EW
	O(5)-H(28)...O(2)	0.99(3)	1.57(3)	2.5599(19)	175(2)		
6	O(1)-H(20)...O(4)	1.10(3)	1.45(3)	2.5455(14)	172(2)		EW
	O(5)-H(21)...O(3)	1.00(2)	1.57(2)	2.5641(13)	176(2)		
7	O(1H)-H(1H)...O(4F)	1.00(3)	1.54(3)	2.5432(15)	174(3)		EW
	O(4I)-H(1I)...O(2E)#12	0.93(3)	1.60(3)	2.5266(15)	171(3)	#12 x+1,y,z	
	O(3J)-H(1J)...O(1K)	0.96(3)	1.59(3)	2.5392(15)	167(3)		
	O(2G)-H(5G)...O(3F)	0.97(3)	1.58(3)	2.5460(15)	176(2)		
	O(2D)-H(1D)...O(1E)	1.02(3)	1.51(3)	2.5308(15)	174(3)		
	O(3L)-H(1L)...O(2K)	0.97(3)	1.54(3)	2.5115(17)	177(3)		
8	O(5)-H(22)...O(2)#4	0.99(2)	1.52(2)	2.4861(11)	166(2)	#4 x,-y+5/2,z-1/2	EW

*****CAHBs are formed between an acid co-former carboxylate and hydroxyl group of a neighbouring acid co-former.

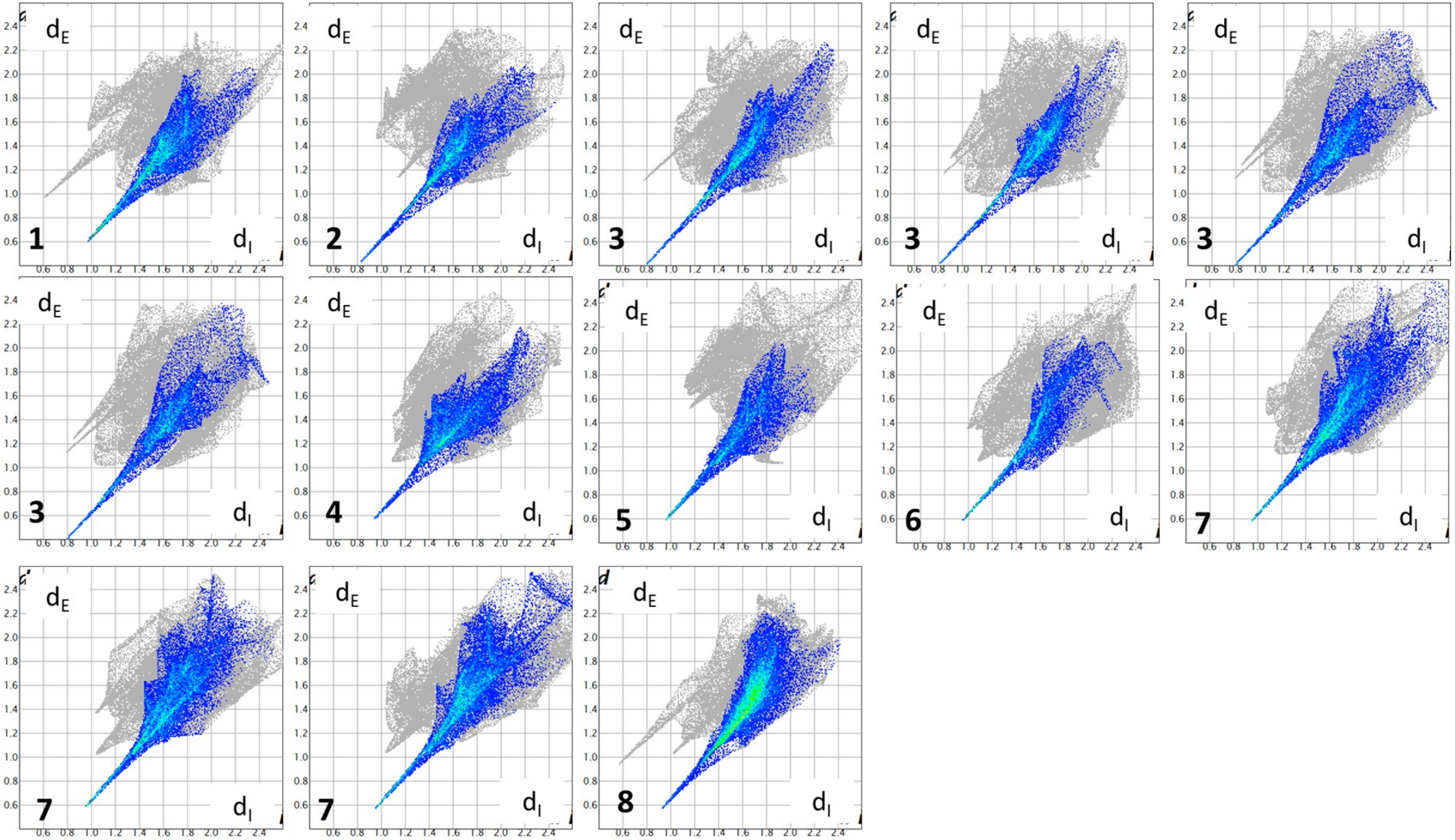

Fig. S1 Fingerprint plots generated in CrystalExplorer[2] from Hirshfeld Surfaces of the deprotonated acids (acceptor end) forming the CAHB motifs in complexes **1** – **8**. Plots are a visual representation of Table S4. Fingerprint plots give a summary in two-dimensions of intermolecular contacts in a crystal, plotting distances from the Hirshfeld surface (a molecular electron density envelop) of a molecule to the nearest internal (d_I) or external (d_E) atom. [3] These plots show the spikes (blue to green) characteristic of HBs involving the acceptor (carboxylate oxygen here). Longer spikes (extending further towards the bottom left of each plot) indicate shorter HBs (seen in **1** – **4**) whilst shorter spikes indicate longer HBs (seen in **5** – **8**).

Table S4 Angles within the DIMER^{-} hydrogen bonded motif in each DMAN molecular complex including the torsion angle of the carboxyl and carboxylate groups forming the O—H···O^{-} CAHBs (ϴ1) and the co-planarity of the benzene rings of each acid co-former (ϴ2).

Complex	DIMER^{-}	ϴ1 (°)	ϴ2 (°)
1	-	–7.25(8)	87.29
2	-	79.17(4)	85.37
3	C71H, C78I	176.1(3)	10.64
	C64G, C64G	-180.0(1)	0.81
	C57F, C57F	180.0(1)	0.81
	C50E, C43D	-161.6(1)	13.75
4	-	–92.67(6)	88.75

Table S5 Angular variation within the TRIMER^{-}/(ACID^{-})$_{n}$ hydrogen bonded motif in each DMAN molecular complex including the torsion angle of the carboxyl and carboxylate groups forming the O—H···O^{-} CAHBs (ϴ1), the co-planarity of the benzene rings of the deprotonated benzoic acid and each protonated acid (ϴ2) and the co-planarity of the two protonated benzoic acid molecules (ϴ3).

Complex	ϴ1 (°)	ϴ2 (°)	ϴ3 (°)
5	42.91(7)	32.93	83.09
	139.79(7)	79.77	
6	101.6(2)	82.02	8.06
	100.7(1)	89.84	
7	(H1B) C1E C1D -87.43(7) C1E C5I -110.13(7)	C1E C1D 79.08 C1E C5I 83.43	C1D C5I 4.53
	(H1C) C1K C1L 96.49(7) C1K C1J 97.66(8)	C1K C1L 72.11 C1K C1J 80.44	C1L C1J 8.68
	(H1A) C1F C1G 100.51(6) C1F C1H 82.04(6)	C1F C1G 76.49 C1F C1H 70.65	C1G C1H 6.16
8	-77.15(4)	60.59	-

Table S6 The weak C—H···X^- HB interactions forming the $[Me_2N_1—H\cdots N_2Me_2]^+\cdots X^-$ fragment across the molecular complexes. $N(CH_3)_2$ group 1 is N_1, the most 'protonated' N of the IHB.

Complex	$N(CH_3)_2$ group	Interaction	dC—H (Å)	dH···X^- (Å)	dC···X^- (Å)	<CHX^- (°)	Sym. Op
1	1	C(12)-H(11)...O(1)	0.990(18)	2.598(18)	3.466(2)	146.4(13)	
	2	C(13)-H(12)...O(3)	0.94(2)	2.54(2)	3.400(2)	152.5(16)	
		C(13)-H(16)...O(5)#2	0.980(19)	2.586(18)	3.241(2)	124.3(13)	#2 x,-y+1/2,z-1/2
2	1	C(11)-H(11)...O(1)	0.984(17)	2.521(17)	3.2031(17)	126.3(12)	
		C(11)-H(12)...O(3)#4	0.977(19)	2.535(18)	3.1200(15)	118.4(13)	#4 -x+1,-y+1,-z+1
		C(12)-H(8)...O(1)	0.975(15)	2.422(16)	3.1051(17)	126.7(12)	
	2	C(13)-H(17)...O(1)	0.971(15)	2.477(16)	3.1485(16)	126.2(12)	
3	1A	C(12)-H(12C)...O(10)	0.96	2.61	3.509(4)	156.0	
		C(11)-H(11A)...O(12)	0.96	2.48	3.306(4)	143.8	
	1B	C(15)-H(15B)...O(8)#10	0.96	2.61	3.552(4)	167.3	#10 -x,-y+1,-z+1
		C(16)-H(16A)...O(8)#11	0.96	2.35	3.230(5)	152.2	#11 x,y+1,z
	2B	C(17)-H(17B)...O(1)#12	0.96	2.50	3.335(5)	145.8	#12 x+1,y+1,z-1
	1C	C(41)-H(41A)...O(11)	0.96	2.51	3.356(5)	147.1	
	2C	C(30)-H(30A)...O(10)	0.96	2.38	3.310(4)	162.5	
4	1	C(14)-H(11)...O(1)	0.998(19)	2.391(19)	3.083(2)	125.8(14)	
	2	C(12)-H(15)...O(1)	1.001(19)	2.509(18)	3.196(2)	125.5(13)	
		C(11)-H(17)...O(1)	0.996(19)	2.636(18)	3.301(2)	124.2(13)	
		C(11)-H(17)...O(4)	0.996(19)	2.616(18)	3.242(2)	120.9(13)	
5	2	C(13)-H(9)...O(2)#1	0.98(2)	2.58(2)	3.391(3)	140.0(16)	#1 -x+1,y-1/2,-z+3/2
		C(13)-H(7)...O(6)#1	1.03(3)	2.51(2)	3.198(3)	123.9(17)	#1 -x+1,y-1/2,-z+3/2
		C(14)-H(16)...O(5)	1.00(3)	2.59(2)	3.250(3)	123.7(17)	
		C(14)-H(16)...O(2)	1.00(3)	2.48(3)	3.471(3)	171.1(19)	
6	1	C(11)-H(10)...N(3)#1	1.002(18)	2.598(18)	3.403(2)	137.3(13)	#1 -x, y-1/2, -z-1/2
		C(11)-H(9)...O(1)#2	0.99(2)	2.49(2)	3.467(2)	168.6(16)	#2 x, y-1, z
		C(12)-H(13)...O(3)	1.017(19)	2.549(19)	3.4751(18)	151.3(14)	
		C(12)-H(12)...O(2)	1.01(2)	2.54(2)	3.2627(18)	128.0(14)	
	2	C(13)-H(14)...O(3)	1.01(2)	2.54(2)	3.519(2)	161.7(16)	

Table S7 The weak C—H···X^- HB interactions forming the $[Me_2N_1—H···N_2Me_2]^+···X^-$ fragment across the molecular complexes. $N(CH_3)_2$ group 1 is N_1, the most 'protonated' N of the IHB.

Complex	$N(CH_3)_2$ group	Interaction	dC—H (Å)	dH···X^- (Å)	dC···X^- (Å)	<CHX^- (°)	Sym. Op
7	1A	C(13A)-H(11A)...O(2F)#5	0.94(2)	2.52(2)	3.411(2)	156.7(15)	#5 -x+1,-y,-z
		C(13A)-H(13A)...O(1G)	0.97(2)	2.41(2)	3.293(2)	151.3(15)	
		C(14A)-H(10A)...O(2F)#5	1.01(2)	2.47(2)	3.409(2)	153.9(16)	#5 -x+1,-y,-z
		C(14A)-H(8A)...O(2I)#11	1.01(2)	2.52(2)	3.388(2)	143.7(17)	#11 -x+2,-y+1,-z+1
		C(14A)-H(9A)...O(4I)	0.96(2)	2.54(2)	3.431(2)	153.7(18)	
	2A	C(12A)-H(16A)...O(1G)	1.02(2)	2.50(2)	3.437(2)	152.8(18)	
		C(12A)-H(14A)...O(1F)#5	0.99(2)	2.49(2)	3.346(2)	143.9(17)	#5 -x+1,-y,-z
	1B	C(11B)-H(8B)...O(4E)#2	0.99(2)	2.45(2)	3.333(2)	148.9(15)	#2 -x,-y+1,-z
		C(13B)-H(11B)...O(4E)#2	0.98(2)	2.45(2)	3.351(2)	152.2(16)	#2 -x,-y+1,-z
		C(13B)-H(12B)...O(4L)#6	0.98(2)	2.45(2)	3.380(2)	159.4(15)	#6 x-1,y,z
		C(11B)-H(9B)...O(2H)#7	0.95(2)	2.32(2)	3.233(2)	163.0(17)	#7 x,y+1,z
		C(13B)-H(13B)...O(3J)#6	1.02(2)	2.60(2)	3.2798(19)	123.5(15)	#6 x-1,y,z
	2B	C(15B)-H(18B)...O(2H)#7	1.03(2)	2.55(2)	3.541(2)	161.1(16)	#7 x,y+1,z
	1C	C(11C)-H(13C)...O(4J)#2	0.97(2)	2.34(2)	3.254(2)	156.7(16)	#2 -x,-y+1,-z
		C(12C)-H(9C)...O(3K)#6	0.98(2)	2.51(2)	3.467(2)	165.7(17)	#6 x-1,y,z
		C(12C)-H(10C)...O(3I)#8	0.99(2)	2.52(2)	3.180(2)	123.7(15)	#8 -x+1,-y+1,-z
		C(11C)-H(12C)...O(3H)#9	0.99(2)	2.63(2)	3.405(2)	135.1(15)	#9 x-1,y,z-1
		C(12C)-H(8C)...O(2D)#2	0.97(2)	2.56(2)	3.508(2)	168.9(16)	#2 -x,-y+1,-z
	2C	C(13C)-H(19C)...O(4J)#2	1.00(2)	2.52(2)	3.477(2)	158.7(18)	#2 -x,-y+1,-z
		C(14C)-H(15C)...O(4K)#6	1.00(2)	2.65(2)	3.472(2)	138.9(17)	#6 x-1,y,z
8	1	C(11)-H(15)...O(2)#2	0.962(16)	2.368(17)	3.2847(14)	159.1(13)	#2 -x,y-1/2,-z+1/2
		C(11)-H(14)...O(4)	0.982(15)	2.538(15)	3.3734(15)	142.9(11)	
		C(12)-H(18)...O(4)	0.968(18)	2.556(18)	3.3930(15)	144.8(13)	
	2	C(13)-H(8)...O(1)	0.960(15)	2.650(16)	3.5590(15)	158.0(12)	
		C(14)-H(11)...O(1)#3	0.981(15)	2.579(15)	3.4458(15)	147.3(12)	#3 x+1,y,z
9	1	C(14)-H(12)...O(1)	0.986(16)	2.467(16)	3.3910(15)	155.9(12)	
		C(14)-H(11)...O(1)#1	0.960(15)	2.335(15)	3.2340(15)	155.8(12)	#1 -x+2,-y+1,-z+1
		C(13)-H(10)...O(2)	0.963(16)	2.605(16)	3.2854(16)	127.9(12)	
		C(13)-H(10)...O(1)	0.963(16)	2.536(16)	3.4051(15)	150.2(12)	
	2	C(11)-H(14)...O(2)	0.979(16)	2.515(16)	3.2376(15)	130.5(12)	
		C(12)-H(17)...O(2)	0.986(16)	2.469(16)	3.1954(16)	130.3(12)	

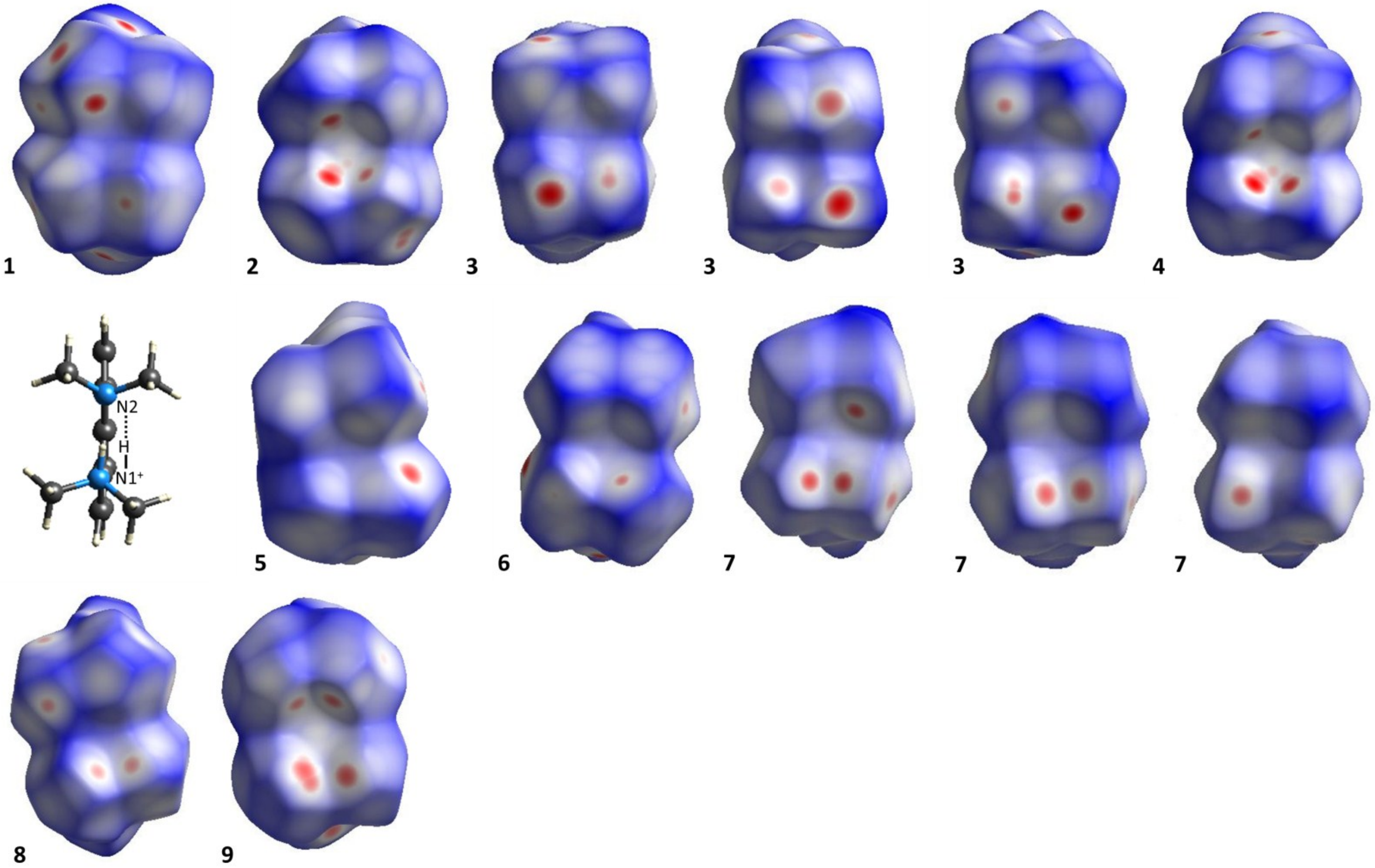

Fig. S2 Hirshfeld surfaces for DMANH$^+$ cations dimethylamino groups in molecular complexes **1** – **9** generated using CrystalExplorer. [1, 2] This surface shows a three-dimensional picture of intermolecular close-contacts in terms of van der Waals (vdW) radii. [4] Red highlights those contacts shorter than the vdW radius, white indicates those around the vdW separation and blue is for longer contacts greater than the vdW separations. Here, red spots are larger and greater in number around the methyl groups of the DMANH$^+$ cation for **1** – **4** (ED) than **5** – **9** (EW), in agreement with interactions to these groups being shorter in general for the ED complexes. In the complexes, close contacts form most often to the protonated dimethylamino group shown by the increasing number of red spots to the protonated side of the cation.

Table S8 The parameters of the [N—H···N]$^+$ IHB formed on DMAN protonation in each molecular complex.

Complex	Interaction	dN—H (Å)	dH···N (Å)	dN···N (Å)	<NHN (°)
1	N(1)-H(1)...N(2)	1.25(2)	1.35(2)	2.5661(19)	161.8(17)
2	N(1)-H(1)...N(2)	1.12(2)	1.51(2)	2.5875(13)	158.0(17)
3	N(1)-H(1A)...N(2)	1.30(3)	1.31(3)	2.563(4)	158(2)
	N(4)-H(1B)...N(3)	1.23(4)	1.37(4)	2.564(4)	161(3)
	N(6)-H(1C)...N(5)	1.16(5)	1.44(5)	2.569(4)	162(3)
4	N(1)-H(1)...N(2)	1.13(2)	1.49(2)	2.5881(19)	159.9(19)
5	N(2)-H(1)...N(1)	1.23(3)	1.38(3)	2.555(2)	157(2)
6	N(1)-H(1)...N(2)	1.095(19)	1.543(19)	2.5916(15)	158.2(17)
7	N(1A)-H(1A)...N(2A)	1.01(2)	1.64(2)	2.6012(19)	157.4(19)
	N(1B)-H(1)...N(2B)	0.99(2)	1.66(2)	2.6007(18)	157(2)
	N(1C)-H(1C)...N(2C)	1.05(2)	1.60(2)	2.5965(18)	156.7(19)
8	N(1)-H(1)...N(2)	1.20(2)	1.43(2)	2.5716(12)	155.4(19)
9	N(1)-H(1)...N(2)	1.022(17)	1.666(17)	2.6196(13)	153.2(15)

Table S9 The C—C bond lengths (Å) in the neutral DMAN[5] and in the $DMANH^+$ cations of the molecular complexes (see Scheme 1 for atom labels).

Complex	C9—C1	C1—C2	C2—C3	C3—C4	C4—C10	C10—C5	C5—C6	C6—C7	C7—C8	C8—C9	C9—C10
DMAN[5]	1.448(1)	1.394(1)	1.413(2)	1.370(2)	1.426(2)	1.419(2)	1.374(2)	1.412(2)	1.390(2)	1.450(1)	1.437(1)
1	1.427(2)	1.363(1)	1.410(2)	1.364(3)	1.421(2)	1.415(2)	1.369(2)	1.410(2)	1.366(2)	1.425(2)	1.434(2)
2	1.430(2)	1.367(2)	1.407(2)	1.363(2)	1.417(2)	1.418(2)	1.365(2)	1.410(2)	1.376(2)	1.427(2)	1.428(2)
3	A 1.421(4)	1.372(7)	1.408(6)	1.359(6)	1.418(7)	1.413(4)	1.360(7)	1.400(5)	1.356(4)	1.439(6)	1.433(5)
	B 1.414(4)	1.365(6)	1.399(6)	1.352(6)	1.429(7)	1.413(5)	1.366(7)	1.411(6)	1.362(4)	1.430(6)	1.424(5)
	C 1.433(6)	1.358(4)	1.404(6)	1.362(7)	1.407(4)	1.422(7)	1.356(5)	1.395(5)	1.373(7)	1.414(4)	1.428(5)
4	1.425(2)	1.358(3)	1.403(2)	1.358(3)	1.414(3)	1.412(2)	1.356(3)	1.408(3)	1.366(2)	1.422(2)	1.432(2)
5	1.425(3)	1.364(3)	1.402(3)	1.356(3)	1.419(3)	1.413(3)	1.363(3)	1.411(3)	1.357(3)	1.426(3)	1.429(3)
6	1.422(2)	1.364(2)	1.405(2)	1.361(2)	1.414(2)	1.416(3)	1.361(2)	1.406(2)	1.367(3)	1.425(2)	1.428(2)
7	H1A 1.421(2)	1.366(2)	1.407(3)	1.356(3)	1.416(3)	1.416(3)	1.352(3)	1.412(3)	1.369(3)	1.422(2)	1.431(2)
	H1B 1.427(2)	1.365(2)	1.407(3)	1.362(3)	1.415(2)	1.416(2)	1.361(3)	1.413(3)	1.370(2)	1.423(2)	1.432(2)
	H1C 1.425(2)	1.367(2)	1.408(3)	1.365(3)	1.416(2)	1.417(2)	1.359(3)	1.411(3)	1.372(3)	1.425(2)	1.432(2)
8	1.423(1)	1.374(2)	1.410(2)	1.368(2)	1.419(2)	1.416(1)	1.368(2)	1.411(2)	1.370(1)	1.430(1)	1.426(1)
9	1.424(2)	1.369(2)	1.410(2)	1.366(2)	1.414(2)	1.415(2)	1.363(2)	1.409(2)	1.374(2)	1.430(2)	1.434(2)

Table S10 The C—N *peri*-amino bond lengths (Å) and < angles (°) in the neutral DMAN[5] and in the $DMANH^+$ cations of the molecular complexes (see Scheme 1 for atom labels).

Complex	C1—N1	C2—N8	<C2C1C9	<C9C8C7	<N1C1C9	< N2C8C9	<CN1C	<CN2C
DMAN[5]	1.402(1)	1.405(2)	119.09(9)	118.8(1)	120.57(9)	120.74(9)	111.92(9)	112.4(1)
1	1.470(2)	1.465(2)	121.5(2)	121.1(2)	117.8(1)	118.2(1)	111.3(1)	110.9(1)
2	1.469(1)	1.455(2)	122.1(1)	121.0(1)	118.35(9)	118.17(9)	111.4(1)	111.05(9)
3	H1A 1.464(5)	1.466(5)	121.4(4)	121.1(3)	117.8(3)	117.2(3)	111.7(3)	111.1(3)
	H1B 1.472(5)	1.460(5)	121.9(4)	121.8(3)	118.3(3)	117.7(3)	112.2(3)	112.0(3)
	H1C 1.469(5)	1.460(5)	122.0(3)	121.3(3)	117.8(3)	118.1(3)	112.2(3)	110.9(3)
4	1.473(2)	1.460(2)	121.7(2)	121.0(2)	118.4(1)	118.4(1)	111.0(1)	111.2(1)
5	1.464(3)	1.462(2)	121.5(2)	121.3(2)	117.7(2)	117.4(2)	111.4(2)	112.3(2)
6	1.469(1)	1.454(2)	122.0(1)	120.7(1)	118.4(1)	118.6(1)	111.7(1)	111.6(1)
7	H1A 1.475(2)	1.460(2)	122.1(2)	120.5(2)	118.7(1)	118.7(1)	112.3(1)	111.8(2)
	H1B 1.469(2)	1.457(2)	122.3(1)	120.5(1)	118.4(1)	118.9(1)	112.3(1)	112.1(1)
	H1C 1.471(2)	1.457(2)	122.2(1)	120.2(2)	118.4(1)	118.8(1)	112.0(1)	111.8(1)
8	1.468(1)	1.462(1)	121.8(1)	121.22(9)	117.47(9)	117.61(8)	111.62(9)	110.79(8)
9	1.473(1)	1.455(1)	122.2(1)	120.6(1)	118.89(9)	118.40(9)	111.39(9)	110.9(1)

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