Electronic Supplementary Information for "Halogen transfer through halogen bonds in halogen-bound ammonia homodimers"

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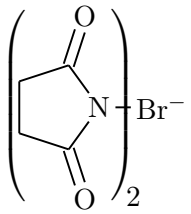
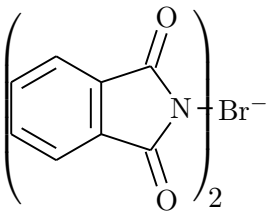
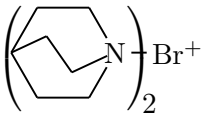
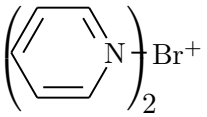
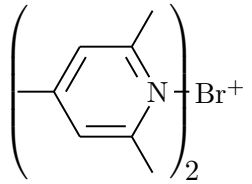
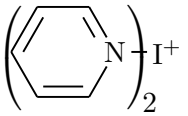
Table S1: Covalent[3] and van der Waals[2] radii for the elements relevant to this work.

Element	r_{cov}/Å	r_{vdw}/Å
H	0.31	1.20
C	0.76	1.70
N	0.71	1.55
F	0.57	1.47
Cl	1.02	1.75
Br	1.20	1.85
I	1.39	1.98

Table S2: X-Ray structural parameters for compounds containing an N-X-N atom arrangement (X = Br or I). Bond distances in Å and bond angles in degrees.

	d(N-X)	∠NXN	ref
	2.110	177.3	[5]
	2.105	176.0	[6]
	2.156[a] 2.120	180	[1]
	2.075[a] 2.107	178.4	[8]
	2.143[a] 2.186	176.3	[8]
$(H_3CCN)_2I^+$	2.198	180.0	[4]
	2.16		[7]

[a]Non-symmetric N−X−N atom arrangement

Table S3: Cartesian coordinates of the optimized geometries of ammonia, N-haloamines (NH_2X) and their corresponding protonated forms (NH_3X^+, X = F, Cl, Br, I) at the MP2(full)/aug-cc-pVTZ-PP level of theory.

NH_3	x	y	z				
N	0.00000	0.00000	0.11248				
H	0.00000	0.93725	-0.26245				
H	-0.81168	-0.46862	-0.26245				
H	0.81168	-0.46862	-0.26245				
H_2NF				H_3NF^+			
N	-0.06454	0.68693	0.00000	N	0.00000	0.00000	-0.59433
F	-0.06454	-0.73214	0.00000	F	0.00000	0.00000	0.76346
H	0.51632	0.89037	0.80715	H	0.00000	0.97828	-0.90362
H	0.51632	0.89037	-0.80715	H	-0.84722	-0.48914	-0.90362
				H	0.84722	-0.48914	-0.90362
H_2NCl				H_3NCl^+			
N	-0.04299	1.11908	0.00000	N	1.05212	0.00000	0.00000
Cl	-0.04299	-0.62150	0.00000	Cl	-0.67826	0.00000	0.00000
H	0.51582	1.36596	0.80858	H	1.38856	0.83765	-0.48079
H	0.51582	1.36596	-0.80858	H	1.38856	-0.83520	-0.48504
				H	1.38855	-0.00245	0.96582
H_2NBr				H_3NBr^+			
N	-0.02559	1.47852	0.00000	N	0.45229	0.24081	1.34323
Br	-0.02559	-0.39412	0.00000	Br	-0.13837	-0.07368	-0.41095
H	0.53741	1.72234	0.80708	H	-0.34673	0.22403	1.97838
H	0.53741	1.72234	-0.80708	H	0.90617	1.15402	1.38978
				H	1.11760	-0.48513	1.61245
H_2NI				H_3NI^+			
N	-0.01815	1.75109	0.00000	N	0.00000	0.00000	-1.74468
I	-0.01815	-0.30680	0.00000	I	0.00000	0.00000	0.34896
H	0.54438	2.00145	0.80678	H	0.00000	0.95773	-2.09395
H	0.54438	2.00145	-0.80678	H	0.82942	-0.47887	-2.09395
				H	-0.82942	-0.47887	-2.09395

Table S4: Cartesian coordinates of the optimized geometries of ammonia-haloamine complexes ([H_2N−X····NH_3], X = F, Cl, Br, I) at the MP2(full)/aug-cc-pVTZ-PP level of theory.

H_2N−Cl····NH_3			
N	-2.10883	0.00001	0.24788
H	-2.46988	0.80753	-0.24659
H	-2.46989	-0.80752	-0.24658
Cl	-0.40342	-0.00001	-0.12026
N	2.57716	0.00000	0.00041
H	2.50688	-0.81110	0.59782
H	2.50682	0.81109	0.59783
H	3.50581	0.00004	-0.39605
H_2N−Br····NH_3			
N	0.17762	2.09375	0.00000
H	-0.35835	2.39563	0.80553
H	-0.35835	2.39563	-0.80553
Br	0.00000	0.21578	0.00000
N	-0.06289	-2.58920	0.00000
H	0.43910	-2.91597	-0.81300
H	-0.96459	-3.04362	0.00000
H	0.43910	-2.91597	0.81300
H_2N−I····NH_3			
N	2.21204	0.00001	-0.12026
H	2.50555	0.80522	0.42234
H	2.50556	-0.80519	0.42234
I	0.14008	0.00000	-0.00152
N	-2.68152	0.00001	0.01065
H	-3.07310	-0.00093	0.94176
H	-3.03785	0.81489	-0.46846
H	-3.03778	-0.81395	-0.47007

Table S5: Cartesian coordinates of the optimized geometries of halogen-bound ammonia homodimers ($[H_3NXNH_3]^+$, X = F, Cl, Br, I) at the MP2(full)/aug-cc-pVTZ-PP level of theory.

$[H_3NXNH_3]^+$	x	y	z
$[H_3N{-}F{\cdots}NH_3]^+$			
N	-0.86556	-0.96663	-1.26417
H	-1.62612	-0.38569	-1.62952
H	-0.18637	-1.19544	-1.99613
H	-1.22621	-1.81238	-0.81244
F	-0.21265	-0.23748	-0.31058
N	1.04448	1.16644	1.52549
H	1.43666	2.02662	1.16574
H	1.81782	0.66688	1.94447
H	0.44563	1.43863	2.29388
$[H_3N{-}F{-}NH_3]^+$			
N	1.79887	0.00000	0.00000
H	2.01642	0.75274	-0.63952
H	2.01642	0.17747	0.97165
H	2.01642	-0.93021	-0.33214
F	0.00000	0.00000	0.00000
N	-1.79887	0.00000	0.00000
H	-2.01642	0.93021	0.33213
H	-2.01642	-0.75274	0.63952
H	-2.01642	-0.17747	-0.97165
$[H_3N{-}Cl{-}NH_3]^+$			
N	0.00000	0.00000	-1.99905
H	0.83924	-0.46299	-2.33149
H	-0.82058	-0.49531	-2.33149
H	-0.01866	0.95829	-2.33149
Cl	0.00000	0.00000	0.00000
N	0.00000	0.00000	1.99905
H	0.82057	0.49531	2.33149
H	0.01867	-0.95829	2.33149
H	-0.83924	0.46298	2.33149
$[H_3N{-}Br{-}NH_3]^+$			
N	0.00000	0.00000	2.10331
H	0.00003	0.95382	2.44861
H	-0.82605	-0.47689	2.44861
H	0.82602	-0.47694	2.44861
Br	0.00000	0.00000	0.00000
N	0.00000	0.00000	-2.10331
H	0.82605	-0.47689	-2.44861
H	-0.00003	0.95382	-2.44861
H	-0.82602	-0.47694	-2.44861

Table S5 – *Continued from previous page*

$[H_3NXNH_3]^+$	x	y	z
$[H_3N{-}I{-}NH_3]^+$			
N	0.00000	0.00000	2.27997
H	-0.47416	0.82136	2.64111
H	-0.47424	-0.82132	2.64111
H	0.94840	-0.00004	2.64111
I	0.00000	0.00000	0.00000
N	0.00000	0.00000	-2.27997
H	0.47416	0.82136	-2.64111
H	0.47424	-0.82132	-2.64111
H	-0.94840	-0.00004	-2.64111

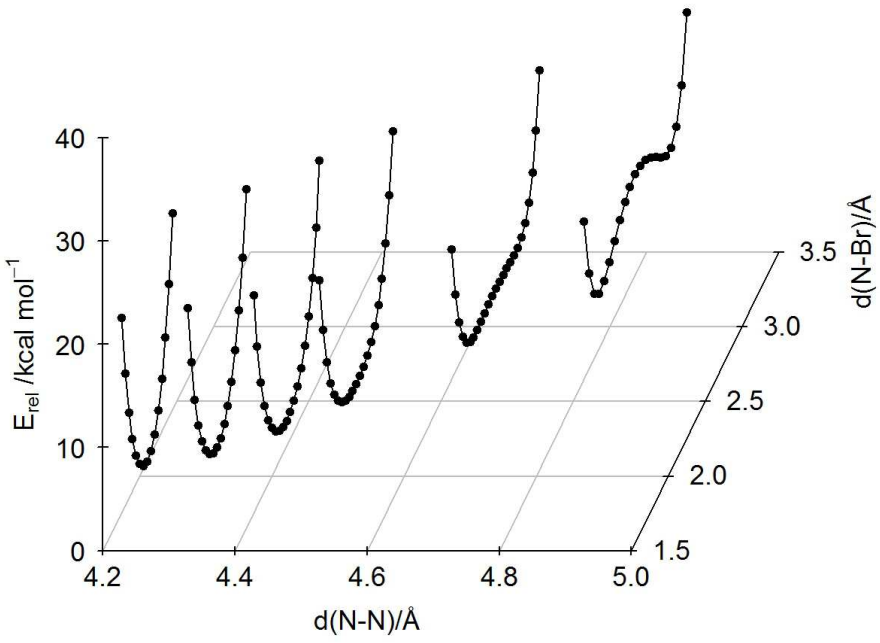


Figure S1: Energy profile for bromine transfer between nitrogen atoms in the $[H_3NBrNH_3]^+$ homodimer.

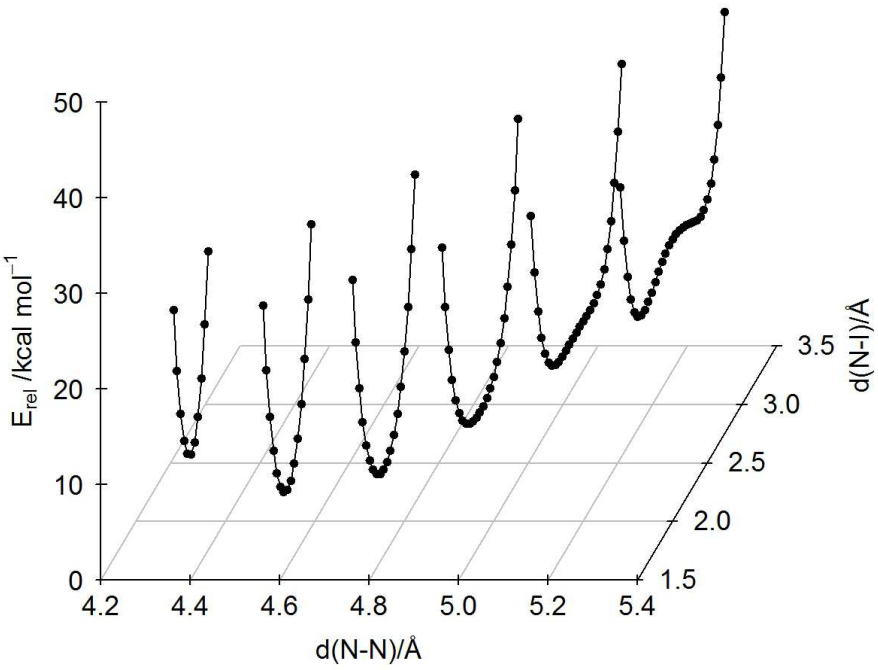


Figure S2: Energy profile for iodine transfer between nitrogen atoms in the $[H_3NINH_3]^+$ homodimer.

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