Supplementary Material (ESI) for *PCCP*

Supporting Information for Ms: B816112G, PCCP (2008)

Interaction of CHX_3 (X = F, Cl, Br) with HNO Induces Remarkable Blue Shifts of both C-H and N-H Bonds

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Table S1: Bond length (r in Å) and their changes (Δr in Å) in the complexes considered

	Isolated Monomers		S1	S2	S3	S4	S5
	CHF_3	HNO	Change (Δr) in Complexes CHF_3···HNO				
r(C4-H5)	1.0876 (1.098)[a]		-0.0017	-0.0021	-0.0019	-0.0025	-0.0025
r(N2-H3)		1.0540 (1.090)[a]	-0.0029	-0.0021	-0.0017	-0.0010	-0.0024
r(C4-F6)	1.3379 (1.332)[a]		0.0084	-0.0025	0.0063	-0.0002	0.0028
r(C4-F7)	1.3379 (1.332)[a]		-0.0016	0.0038	0.0001	0.0031	0.0015
r(C4-F8)	1.3379 (1.332)[a]		-0.0016	0.0038	0.0001	0.0031	0.0015
r(O1═N2)		1.2213 (1.209)[a]	0.0017	0.0012	0.0003	0.0001	0.0018
	$CHCl_3$	HNO	Change (Δr) in complexes $CHCl_3$···HNO				
r(C4-H5)	1.0849 (1.073)[a]		-0.0015	-0.0011	-0.0009	-0.0011	-0.0023
r(N2-H3)		1.0540 (1.090)[a]	-0.0019	-0.0010	-0.0016	-0.0009	-0.0019
r(C4-Cl6)	1.7652 (1.762)[a]		0.0084	-0.0040	0.0062	-0.0026	0.0020
r(C4-Cl7)	1.7652 (1.762)[a]		-0.0019	0.0038	-0.0004	0.0039	0.0008
r(C4-Cl8)	1.7652 (1.762)[a]		-0.0019	0.0038	-0.0004	0.0039	0.0008
r(O1═N2)		1.2213 (1.209)[a]	0.0014	0.0011	0.0004	0.0001	0.0022
	$CHBr_3$	HNO	Change (Δr) in complexes $CHCl_3$···HNO				
r(C4-H5)	1.0852 (1.110)[a]		-0.0012	-0.0009	-0.0004	-0.0008	-0.0019
r(N2-H3)		1.0540 (1.090)[a]	-0.0017	-0.0011	-0.0016	-0.0011	-0.0018
r(C4-Br6)	1.9330 (1.924)[a]		0.0083	-0.0035	0.0061	-0.0028	0.0018
r(C4-Br7)	1.9330 (1.924)[a]		-0.0017	0.0042	-0.0005	0.0041	0.0011
r(C4-Br8)	1.9330 (1.924)[a]		-0.0017	0.0042	-0.0005	0.0041	0.0011
r(O1═N2)		1.2213 (1.209)[a]	0.0016	0.0013	0.0004	0.0003	0.0022

[a]: Experimental values taken from ref. 44.

Table S3: Calculated interaction energies (kJ.mol^{-1}) with BSSE,and both BSSE and ZPE corrections of complexes and distances of hydrogen bond (R, in Å)

		S1	S2	S3	S4	S5
CHF_3···HNO	ΔE(BSSE)	-7.87	-7.19	-9.38	-8.28	-7.87
	ΔE(ZPE+BSSE)	-4.47	-3.47	-5.67	-5.35	-4.92
	R(H5···O1(N2))	2.60	2.67	2.62	2.72	2.45(2.57)[b]
	R(H3···X(6,7,8))	2.39	2.62	2.81	3.08	
	C4H5O1(N2)	120.2	99.4	119.3	100.8	164.2(136.1)[c]
	N2H3X(6,7,8)	129.3	118.7	90.6	81.0	
$CHCl_3$···HNO	ΔE(BSSE)	-7.90	-8.07	-9.79	-9.79	-7.70
	ΔE(ZPE+BSSE)	-4.48	-5.02	-6.57	-6.28	-4.12
	R(H5···O1(N2))	2.36	2.46	2.37	2.45	2.37(2.45)[b]
	R(H3···X(6,7,8))	2.86	3.06	3.41	3.39	
	C4H5O1(N2)	141.4	120.4	143.3	121.0	164.5(135.1)[c]
	N2H3X(6,7,8)	131.1	119.7	86.1	84.5	
$CHBr_3$···HNO	ΔE(BSSE)	-8.91	-9.03	-10.67	-10.97	-8.20
	ΔE(ZPE+BSSE)	-5.65	-6.35	-7.41	-7.72	-5.15
	R(H5···O1(N2))	2.34	2.45	2.33	2.41	2.34(2.47)[b]
	R(H3···X(6,7,8))	3.00	3.18	3.58	3.52	
	C4H5O1(N2)	146.1	125.4	148.7	126.1	168.6(139.2)[c]
	N2H3X(6,7,8)	132.8	121.1	86.3	85.4	

b refers to the H5···N2 distances; c refers to the C4H5N2 angle; the scaling factor for ZPE is 0.97.

Table S5: Selected NBO data (natural charge (e), occupation of σ-antibonding orbitals (e), hybridization (%), lone pair (e) and electron density transfer (e)) in the isolated monomers and their complexes

	Isolated monomers		S1	S2	S3	S4	S5
	CHF_3	HNO	Change (Δ) in Complex CHF_3···HNO				
σ*(C4H5)	0.0613		-0.0009	-0.0015	0	-0.0011	0.0006
σ*(N2H3)		0.0613	-0.0029	-0.0019	-0.0009	-0.0005	-0.0024
%s(C4)	30.30		0.47	0.47	0.62	0.54	0.70
%s(N2)		18.46	0.57	0.45	0.47	0.39	0.57
qC4	0.952		-0.007	-0.006	-0.011	-0.007	-0.012
qN2		-0.013	0.003	0.005	-0.019	-0.018	-0.006
qH5	0.098		0.015	0.014	0.018	0.016	0.015
qH3		0.232	0.016	0.012	0.014	0.012	0.014
n(O1)			-0.001	-0.001	0	-0.001	-0.003
n(N2)			0	0	-0.004	-0.003	-0.006
EDT			0.003	0.003	0.005	0.003	0.009
	$CHCl_3$	HNO	Change (Δ) in Complex $CHCl_3$···HNO				
σ*(C4H5)	0.0648		-0.0016	-0.0012	-0.0001	-0.0009	-0.0010
σ*(N2H3)		0.0613	-0.0014	-0.0009	-0.0003	0	-0.0020
%s(C4)	27.76		0.89	0.64	1.33	0.98	1.07
%s(N2)		18.46	0.50	0.43	0.47	0.43	0.50
qC4	-0.309		-0.004	-0.004	-0.008	-0.005	-0.002
qN2		-0.013	0.007	0.006	-0.021	-0.024	-0.006
qH5	0.189		0.018	0.015	0.024	0.022	0.012
qH3		0.232	0.012	0.010	0.015	0.014	0.014
n(O1)			-0.002	-0.002	-0.001	-0.001	-0.003
n(N2)			0	0	-0.007	-0.005	-0.002
EDT			0.003	0.002	0.009	0.003	0.009
	$CHBr_3$	HNO	Change (Δ) in Complex $CHBr_3$···HNO				
σ*(C4H5)	0.0567		-0.0012	-0.0009	0.0007	-0.0003	-0.0008
σ*(N2H3)		0.0613	-0.0009	-0.0005	-0.0002	-0.0001	-0.0020
%s(C4)	28.70		1.09	0.74	1.69	1.19	1.29
%s(N2)		18.46	0.52	0.46	0.47	0.46	0.45
qC4	-0.561		-0.002	-0.003	-0.005	-0.003	-0.001
qN2		-0.013	0.007	0.005	-0.021	-0.024	-0.004
qH5	0.197		0.017	0.015	0.024	0.022	0.011
qH3		0.232	0.012	0.010	0.015	0.015	0.014
n(O1)			-0.002	-0.002	-0.002	-0.002	-0.004
n(N2)			0	0	-0.009	-0.006	-0.002
EDT			0.003	0.002	0.011	0.004	0.010

a. Cartesian coordinates of monomers and complexes at the MP2/6-311++G(d,p) level

HNO	x	y	z
N	0.17606	0.11894	0.55443
H	0.17754	1.17295	0.55910
O	-0.17624	-0.25069	-0.55502

CHF_3	x	y	z
C	0	0	0.33914
H	0	0	1.42674
F	0	-1.25359	-0.12821
F	1.08564	0.62680	-0.12821
F	-1.08564	0.62680	-0.12821

$CHCl_3$	x	y	z
C	0	0	0.45003
H	0	0	1.53482
Cl	0	-1.68277	-0.08304
Cl	1.45733	0.84139	-0.08304
Cl	-1.45733	0.84139	-0.08304

$CHBr_3$	x	y	z
C	0	0	0.51949
H	0	0	1.60463
Br	0	-1.84870	-0.04497
Br	-1.60102	0.92435	-0.04497
Br	1.60102	0.92435	-0.04497

	F_3CH•••HNO			
	Atom	x	y	z
S1	O	-2.29431	0	0.61983
	N	-2.20543	0	1.83957
	H	-1.18334	0	2.08486
	C	0.70778	0	-0.70877
	H	-0.31681	0	-1.06858
	F	0.72179	0	0.63747
	F	1.36388	-1.08529	-1.12980
	F	1.36388	1.08529	-1.12980
S2	F	0.33748	-0.56666	-1.08368
	F	0.33748	-0.56666	1.08368
	F	2.21943	-0.59196	0
	O	-1.65181	1.43599	0
	N	-2.51995	0.57530	0
	H	-2.04346	-0.36257	0
	C	0.97736	-0.10149	0
	H	0.98392	0.98397	0
S3	O	1.51768	0	-3.04875
	N	1.21167	0	-1.86606
	H	2.09490	0	-1.29398
	C	-0.72358	0	0.79996
	H	-0.87500	0	-0.27510
	F	0.59136	0	1.07882
	F	-1.26798	1.08547	1.36180
	F	-1.26798	-1.08547	1.36180
S4	F	-1.12711	-0.87423	-0.21764
	F	-1.13247	-0.84636	1.95375
	F	0.74905	-0.87423	0.86986
	O	1.24333	2.09282	-2.14500
	N	0.85788	1.14351	-1.48002
	H	1.14284	0.25700	-1.97164
	C	-0.50172	-0.39079	0.86557
	H	-0.48957	0.69401	0.84461
S5	O	2.52919	0	-0.79259
	N	2.49982	0	0.43014
	H	3.49119	0	0.78105
	C	-0.89606	0	-0.05851
	H	0.10256	0	-0.48291
	F	-1.82198	0	-1.02809
	F	-1.08621	1.08605	0.70197
	F	-1.08621	-1.08605	0.70197

	Cl_3CH•••HNO			
	Atom	x	y	z
S1	O	-2.73620	0	0.75754
	N	-2.91104	0	1.96769
	H	-1.96361	0	2.42517
	C	0.31200	0	-0.43831
	H	-0.76668	0	-0.53771
	Cl	0.66845	0	1.29910
	Cl	0.93416	1.45774	-1.21107
	Cl	0.93416	-1.45774	-1.21107
S2	O	-2.64730	0	0.61097
	N	-2.63497	0	1.83335
	H	-1.62871	0	2.14355
	C	0.29363	0	-0.51840
	H	-0.71560	0	-0.91325
	Cl	1.42237	0	-1.87086
	Cl	0.47134	1.45658	0.46951
	Cl	0.47134	-1.45658	0.46951
S3	O	2.16902	0	-3.21074
	N	1.93613	0	-2.01142
	H	2.85268	0	-1.49411
	C	-0.43424	0	0.28293
	H	-0.05422	0	-0.73221
	Cl	0.97628	0	1.35446
	Cl	-1.40279	-1.45800	0.50791
	Cl	-1.40279	1.45800	0.50791
S4	O	2.41228	0	-2.92252
	N	1.86371	0	-1.83120
	H	2.60671	0	-1.08483
	C	-0.55078	0	0.19298
	H	-0.39643	0	-0.87964
	Cl	-2.28358	0	0.51566
	Cl	0.22268	1.45775	0.83056
	Cl	0.22268	-1.45775	0.83056
S5	O	2.88386	0	-1.02935
	N	2.88204	0	0.19420
	H	3.88175	0	0.52218
	C	-0.40697	0	-0.09157
	H	0.56119	0	-0.57583
	Cl	-1.63912	0	-1.35833
	Cl	-0.51121	1.45818	0.89912
	Cl	-0.51121	-1.45818	0.89912

	Br_3CH•••HNO			
	Atom	x	y	z
S1	O	-3.14802	0	0.90591
	N	-3.37359	0	2.10783
	H	-2.44575	0	2.60435
	C	-0.06450	0	-0.25921
	H	-1.14729	0	-0.30954
	Br	0.38972	0	1.62810
	Br	0.55913	-1.60215	-1.13893
	Br	0.55913	1.60215	-1.13893
S2	O	-3.06389	0	0.74755
	N	-3.06458	0	1.97018
	H	-2.06164	0	2.29082
	C	-0.06206	0	-0.37219
	H	-1.09273	0	-0.70891
	Br	0.17078	-1.60089	0.69330
	Br	1.07244	0	-1.93290
	Br	0.17078	1.60089	0.69330
S3	O	-0.06057	0	-0.00258
	N	-0.02037	0	1.21851
	H	0.98822	0	1.51899
	C	-1.93536	0	3.91398
	H	-1.67520	0	2.86084
	Br	-2.95869	1.60193	4.26207
	Br	-2.95869	-1.60193	4.26207
	Br	-0.25421	0	4.88029
S4	O	2.54948	0	-3.39368
	N	2.06903	0	-2.27049
	H	2.85609	0	-1.57107
	C	-0.26690	0	-0.11658
	H	-0.08860	0	-1.18619
	Br	-2.17453	0	0.17716
	Br	0.57233	-1.60273	0.57570
	Br	0.57233	1.60273	0.57570
S5	O	3.42217	0	-0.40906
	N	3.25061	0	0.80233
	H	4.19522	0	1.26590
	C	0.02509	0	-0.14113
	H	1.08341	0	-0.37217
	Br	-0.92170	0	-1.82833
	Br	-0.33287	-1.60308	0.88001
	Br	-0.33287	1.60308	0.88001

b. Energies with ZPE correction of monomers and complexes at the MP2/6-311++G(d,p) level

Table: The ZPE corrected energy of the isolated monomers

	HNO	CHF_3	$CHCl_3$	$CHBr_3$
E(Hartree/particle)	-130.187042	-337.605883	-1417.506764	-7756.050373

Table: The ZPE corrected energy of complexes (E in Hartree/particle)

	S1	S2	S3	S4	S5
F_3CH•••HNO	-467.796405	-467.796840	-467.796389	-467.796618	-467.796199
Cl_3CH•••HNO	-1547.698730	-1547.699559	-1547.699498	-1547.699854	-1547.699036
Br_3CH•••HNO	-7886.242144	-7886.242873	-7886.243005	-7886.243223	-7886.242317

c. The change of some selected papameters in the isolated monomers including bond length (r, in Å), dipole moment of molecule (μ, in Debye), stretching frequency (υ, in cm^{-1}) and infrared intensity (I, in $km.mol^{-1}$)

Table: The change of some characteristic parameters in CHF_3

r(CH)	0.9276	0.9676	1.0076	1.0476	1.0876	1.1276	1.1676	1.2076	1.2476	1.2876
μ	2.0631	2.0535	2.0395	2.0212	1.9987	1.9721	1.9412	1.9062	1.8671	1.8238
υ(CH)	5003.2	4495.6	4033.2	3610.7	3224.0	2869.5	2543.8	2243.2	1964.1	1702.7
I(CH)	11.9	16.5	21.8	27.7	34.3	41.7	49.7	58.4	67.8	77.5

Table: The change of some characteristic parameters in $CHCl_3$

r(CH)	0.9248	0.9648	1.0048	1.0448	1.0848	1.1248	1.1648	1.2048	1.2448	1.2848
μ	1.2713	1.288	1.3011	1.3106	1.3164	1.3182	1.3192	1.3196	1.3198	1.3200
υ(CH)	5025.6	4508.1	4036.9	3606.8	3213.3	2852.5	2520.1	2212.0	1924.1	1652.1
I(CH)	4.9	2.8	1.3	0.3	0.0	0.5	2.0	4.5	8.3	13.3

Table: The change of some characteristic parameters in $CHBr_3$

r(CH)	0.9252	0.9652	1.0052	1.0452	1.0852	1.1252	1.1652	1.2052	1.2452	1.2852
μ	1.0212	1.0441	1.0642	1.0815	1.0958	1.1067	1.1141	1.1176	1.1179	1.1177
υ(CH)	5019.9	4503.1	4033.1	3604.2	3211.9	2852.1	2520.5	2212.9	1925.3	1653.2
I(CH)	13.5	10.4	7.6	5.0	2.9	1.2	0.2	0.0	0.8	2.7