Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Orthogonal interactions between nitryl derivatives and electron donors: Pnictogen bonds

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- **Table S1**. Minimum values of the molecular electrostatic potential (ua) on the 0.001 au electron density isosurface at MP2/aug-cc-pVTZ level, for the electron donors.

- **Table S2**. Comparison between interaction energies at MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ levels for NO_2F complexes.

- **Table S3**. Electron density at the bond critical points (ρ), Laplacian ($\nabla^2\rho$) at MP2/aug-cc-pVTZ computational level. Charge (e) of the nitryl derivative within the complexes calculated with the AIM method at MP2/aug-cc-pVTZ computational level and donation from the Y electron donor to the O-N antibonding orbital ($kJmol^{-1}$) at B3LYP/aug-cc-pVTZ level.

-**Table S4.** ^{15}N chemical shifts (ppm) for NO_2X monomers and complexes at MP2/aug-cc-pVTZ level.

- **Fig. S1**. Molecular electrostatic potential on the 0.001 au isosurface for all the NO_2X monomers. MEP values color scheme: Red > 0.04, Yellow > 0.02, Green > 0.00, Blue < 0.00. Maxima and minima values of MEP are represented by black and cyan dots respectively.

- **Fig. S2**. Molecular graphs obtained with AIM theory for all the XNO_2 complexes.

- **Fig. S3**. NCI plot of the non-covalent interaction all the complexes. Blue areas are those with $\lambda 2 > 0$ (strong attractive), while green ones correspond to $\lambda 2 \approx 0$ (weak). $\lambda 2$ is one of the three eigenvalues of the electron-density Hessian with $\lambda 1 \leq \lambda 2 \leq \lambda 3$.

Table S1. Minimum values of the molecular electrostatic potential (ua) on the 0.001 au electron density isosurface at MP2/aug-cc-pVTZ level, for the electron donors.

	MIN-MEP
NH_3	-0.0637
HNC	-0.0529
H_2O	-0.0515
HCN	-0.0509
HCCH	-0.0233
CO	-0.0223
OC	-0.0065

Table S2. Comparison between interaction energies at MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ levels for NO_2F complexes.

	NO_2F	
	MP2	CCSD(T)
H_3N	–18.9	-17.2
HNC	–14.3	-12.9
H_2O (a)	–17.3	-13.4
H_2O (b)	–	–
HCN	–13.9	-13.3
HCCH	–11.9 (–11.5)[a]	–10.4 (–9.3)[a]
O**C**	–8.2	-8.0
C**O**	–5.0	-5.9

Table S3. Electron density at the bond critical points (ρ), Laplacian ($\nabla^2\rho$) at MP2/aug-cc-pVTZ computational level. Charge (e) of the nitryl derivative within the complexes calculated with the AIM method at MP2/aug-cc-pVTZ computational level and donation from the Y electron donor to the O-N antibonding orbital ($kJmol^{-1}$) at B3LYP/aug-cc-pVTZ level.

	d(X···N)	ρ	$\nabla^2\rho$	Charge of the nitryl derivative	LP Y->σ*O-N
$H_3N\cdots NO_2F$	2.823	0.0117	0.0508	-0.0160	4.3
$H_2O\cdots NO_2F$ (a)	2.740	0.011	0.056	-0.0131	3.6
$HNC\cdots NO_2F$	2.817	0.011	0.051	-0.0187	1.2
$HCN\cdots NO_2F$	2.960	0.010	0.041	-0.0131	1.3
$HCCH\cdots NO_2F$ [a]	3.086	0.008	0.033	-0.0179	0.4

HCCH···NO_2F [b]	3.144	0.007	0.03	-0.0172	2.2
CO···NO_2F	2.862	0.007	0.04	-0.0119	0.6
OC···NO_2F	3.008	0.008	0.037	-0.0020	1
H_3N···NO_2Cl	2.899	0.0111	0.0467	-0.0143	4.2
H_2O···NO_2Cl (a)	2.790	0.010	0.049	0.0001	3
H_2O···NO_2Cl (b)	2.774	0.011	0.053	-0.0086	2.6
HCN···NO_2Cl	2.859	0.010	0.048	-0.0094	1.5
HNC···NO_2Cl	3.014	0.009	0.038	-0.0153	1.3
HCCH···NO_2Cl[a]	3.092	0.008	0.033	-0.0133	0.3
CO···NO_2Cl	2.900	0.007	0.038	-0.0090	0.6
OC···NO_2Cl	3.071	0.007	0.033	0.0006	0.9
H_3N···NO_2Br	2.916	0.0108	0.0447	-0.0120	4.1
HCN···NO_2Br	2.864	0.010	0.047	-0.0078	1.7
H_2O···NO_2Br(a)	2.808	0.009	0.047	0.0050	2.3
H_2O···NO_2Br(b)	2.776	0.011	0.053	-0.0070	2.8
HCCH···NO_2Br[a]	3.085	0.008	0.033	-0.0004	0.3
HNC···NO_2Br	3.026	0.009	0.037	-0.0137	1.5
CO···NO_2Br	3.079	0.007	0.038	-0.0062	0.8
OC···NO_2Br	2.894	0.007	0.033	0.0016	1
H_3N···NO_2-NO_2	2.919	0.011	0.043	-0.0260	4.6
H_2O···NO_2-NO_2	2.773	0.011	0.053	-0.0123	2.8
HCN···NO_2-NO_2	2.884	0.010	0.045	-0.0137	2.1
HCCH···NO_2-NO_2	3.079	0.009	0.033	-0.0224	2.7
HNC···NO_2-NO_2	3.048	0.009	0.035	-0.0204	2.1
CO···NO_2-NO_2	2.948	0.007	0.033	-0.0124	1.3
OC···NO_2-NO_2	3.127	0.007	0.029	-0.0017	0.8
H_3N···NO_2-CN	2.859	0.014	0.047	-0.0292	3.4
H_2O···NO_2-CN	2.734	0.012	0.061	-0.0103	2.7
HCN···NO_2-CN	2.838	0.011	0.054	-0.0124	1.5

HNC···NO_2-CN	2.994	0.010	0.04	-0.0198	1.2
HCCH···NO_2-CN	3.054	0.009	0.036	-0.0206	1.5
CO···NO_2-CN	2.899	0.007	0.039	-0.0115	0.6
OC···NO_2-CN	3.076	0.008	0.035	-0.0011	0.6
H_3N···NO_2-CCH	2.888	0.010	0.045	-0.0116	2
H_2O···NO_2-CCH[b]	2.855	0.010	0.047	-0.0045	1.5
HCN···NO_2-CCH	3.128	0.007	0.033	-0.0049	0.5*
HNC···NO_2-CCH	3.024	0.009	0.036	-0.0118	0.6
HCCH···NO_2-CCH	3.077	0.008	0.034	-0.0129	0.7
CO···NO_2-CCH	2.901	0.007	0.038	-0.0063	0.5
OC···NO_2-CCH	3.066	0.008	0.034	0.0020	0.4
H_3N···NO_2-$CHCH_2$	2.911	0.009	0.043	-0.0064	1.4
HNC···NO_2-$CHCH_2$	3.110	0.008	0.032	-0.0112	0.3
CO···NO_2-$CHCH_2$	2.915	0.007	0.037	-0.0039	0.4
OC···NO_2-$CHCH_2$	3.053	0.008	0.033	0.0029	0.4
H_3N···NO_2-OH	2.902	0.010	0.044	-0.0134	1.6
HCCH··· NO_2-OH	3.100	0.008	0.032	-0.0143	0.4
CO··· NO_2-OH	2.893	0.008	0.036	-0.0085	0.5
OC··· NO_2-OH	3.034	0.007	0.038	-0.0002	0.4

* LPN ➔ σ*CC)

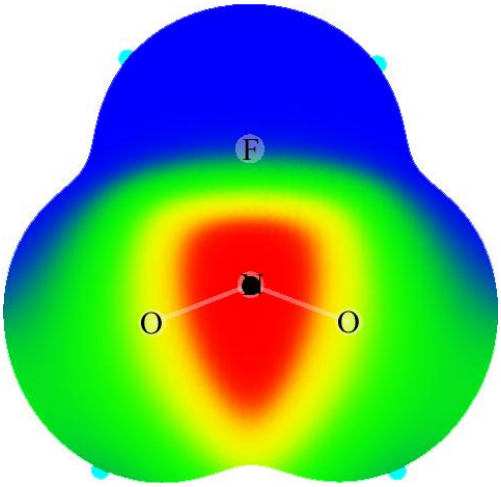
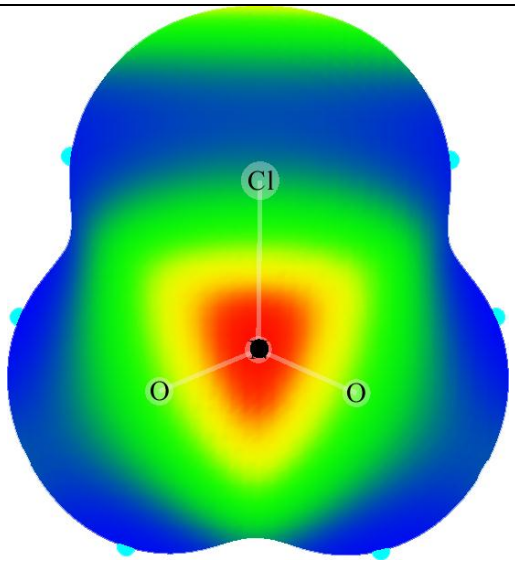
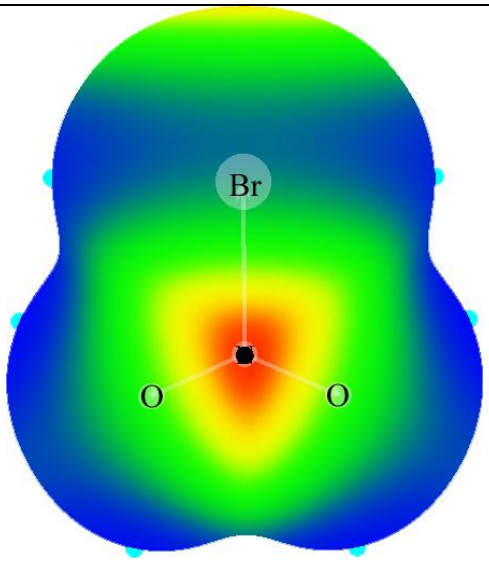
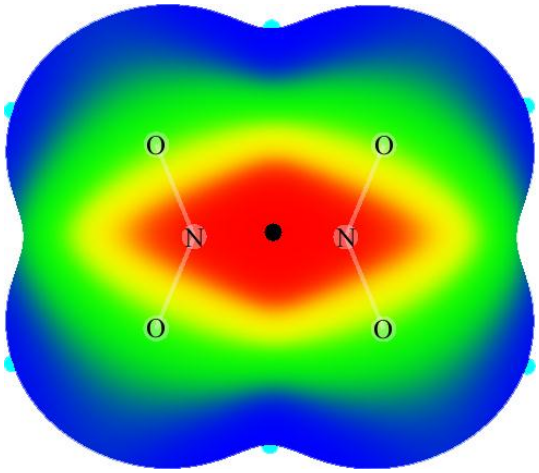
Table S4. ^{15}N chemical shifts (ppm) for NO_2X monomers and complexes at MP2/aug-cc-pVTZ level.

	NO_2CN	NO_2F	NO_2NO_2	NO_2Cl	NO_2Br	NO_2OH	NO_2CCH	NO_2CHCH_2
Monomer	–3.34	–6.99	–69.27	–5.42	–8.05	–29.47	–20.47	–55.03
H_3N		–5.67	–71.49	–7.37	–10.76	–32.07	–25.59	–59.33
HNC	–8.49	–5.85	–71.09	–6.27	–10.12	–	–23.43	–56.62
H_2O (a)	–	–3.79	–	–4.18	–5.90	–	–	–
H_2O (b)	–8.25	–	–70.20	–5.91	–8.90	–	–25.55	–
HCN	–7.73	–6.01	–70.29	–5.89	–9.52	–	–24.21	–
HCCH	–6.48	–5.36 (–5.76)[a]	–70.83	–5.39	–9.19	–28.38	–20.98	–
CO	–6.16	–6.41	–70.93	–6.23	–9.57	–29.07	–21.94	–55.7

OC	–4.19	–6.59	–69.67	–5.59	–8.76	–29.12	–20.61	–54.97

[a] Data in parenthesis corresponds to the parallel structure.

Fig. S1. Molecular electrostatic potential on the 0.001 au isosurface for all the NO_2X monomers. MEP values color scheme: Red > 0.04, Yellow > 0.02, Green > 0.00, Blue < 0.00. Maxima and minima values of MEP are represented by black and cyan dots respectively.

		
	NO_2-F	NO_2-Cl
		
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	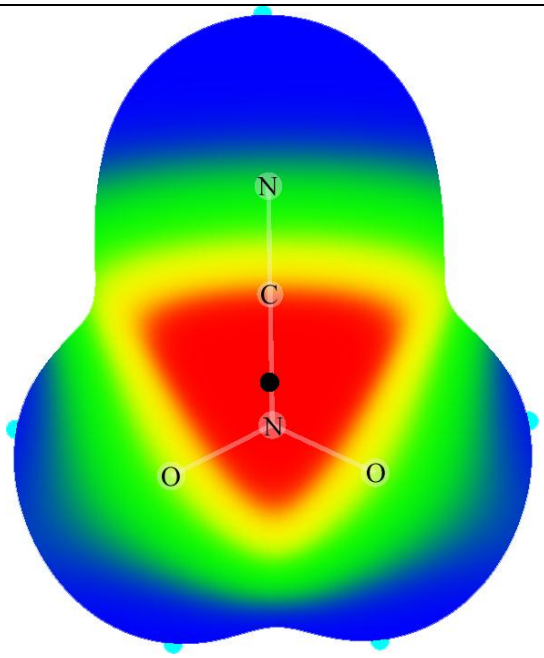	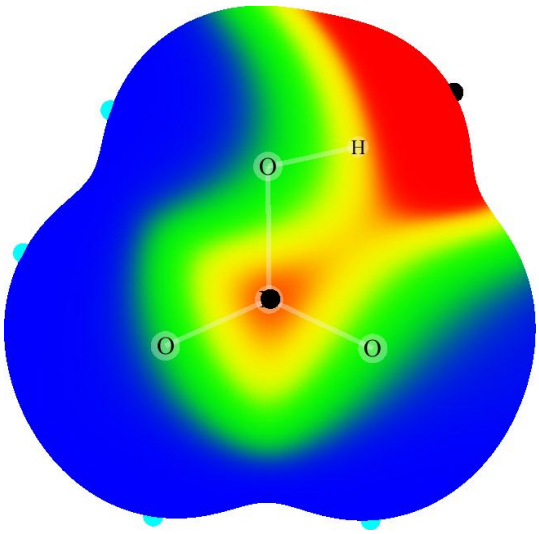
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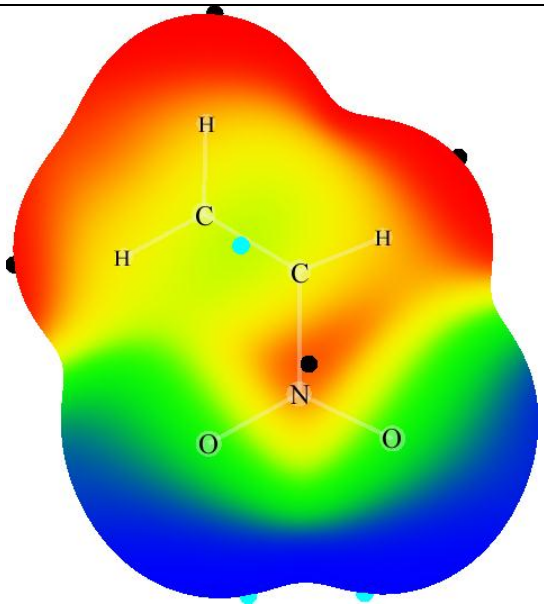
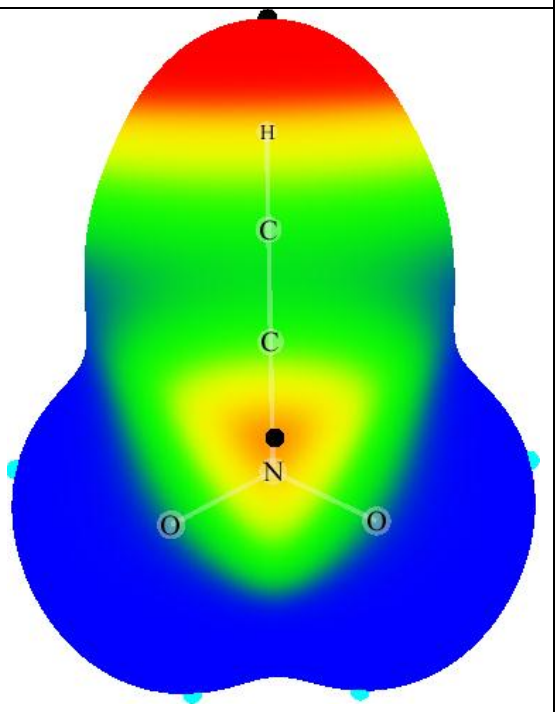
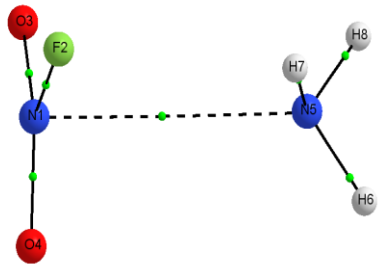
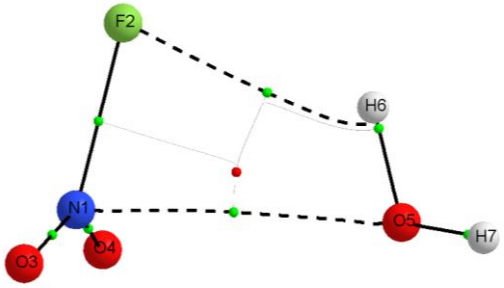
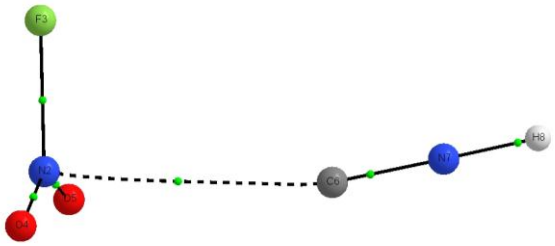
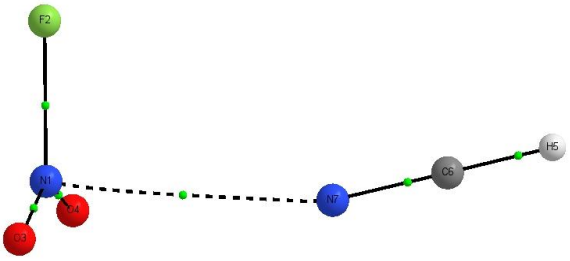
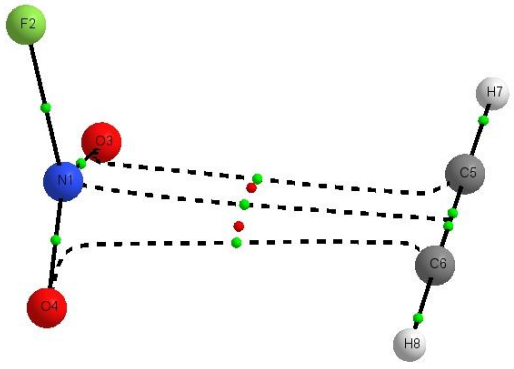
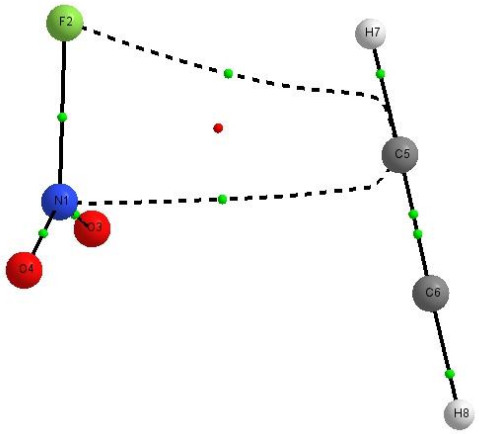
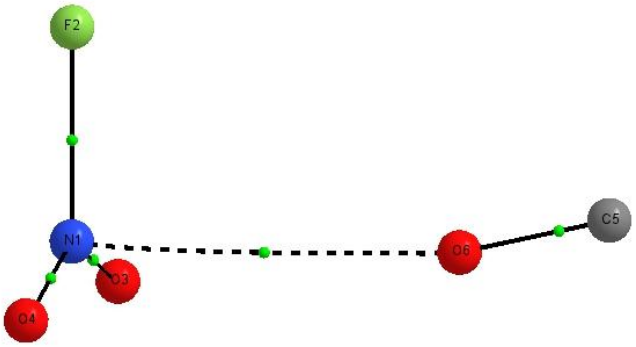
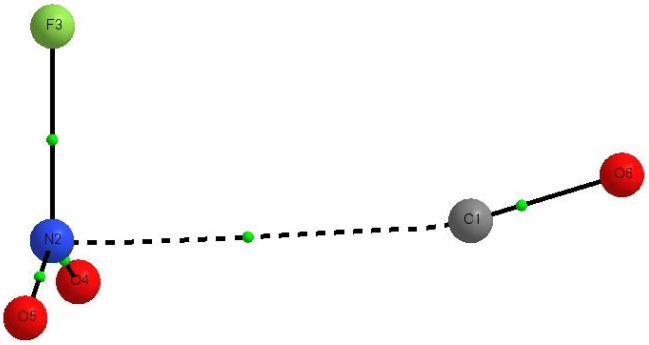
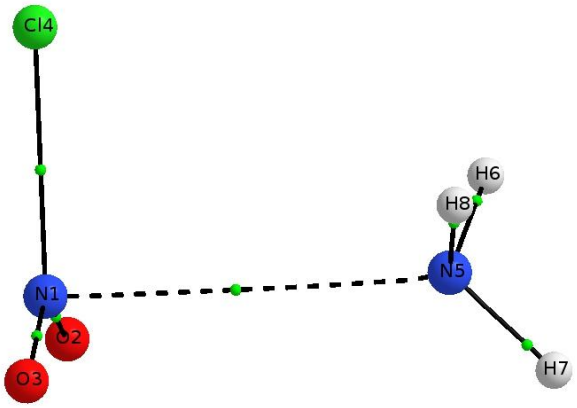
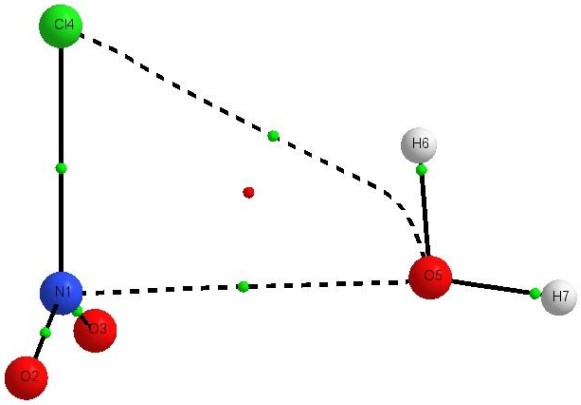
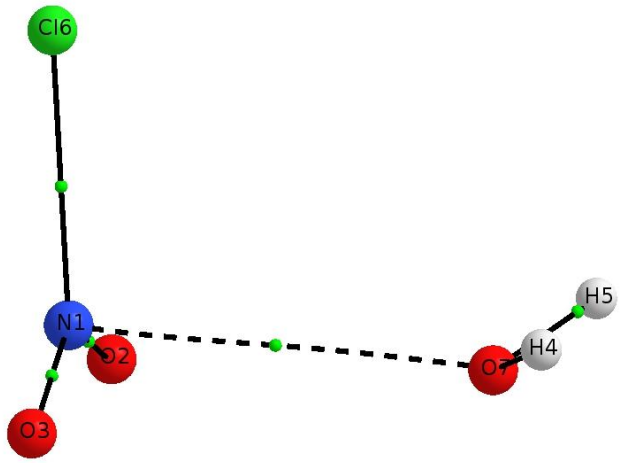
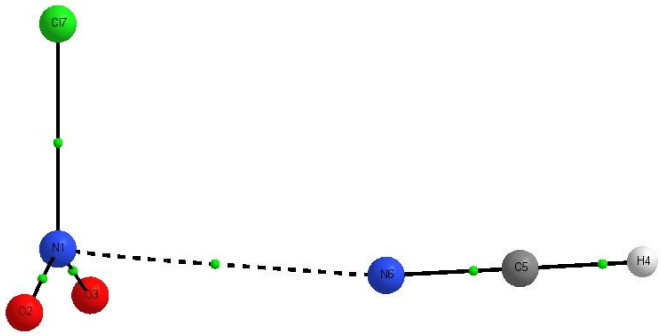
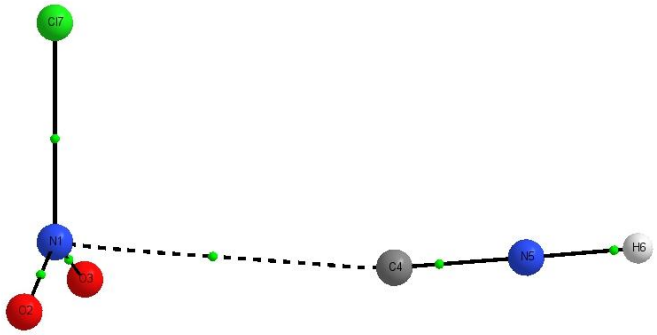
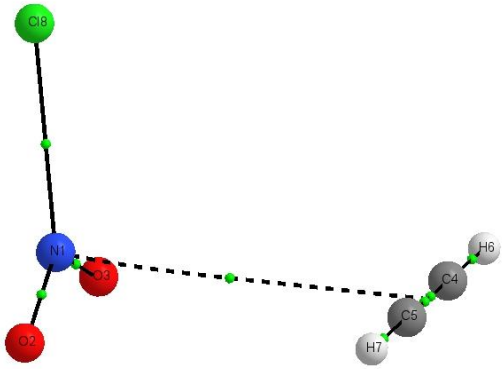
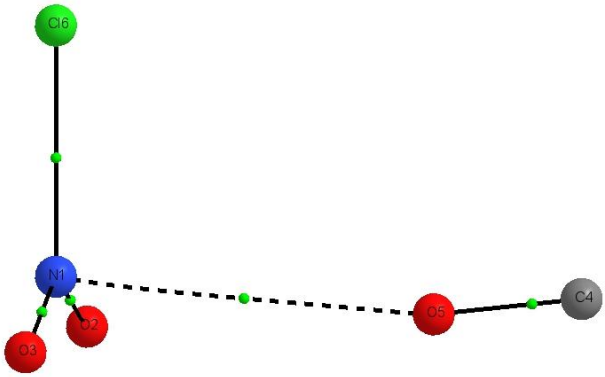
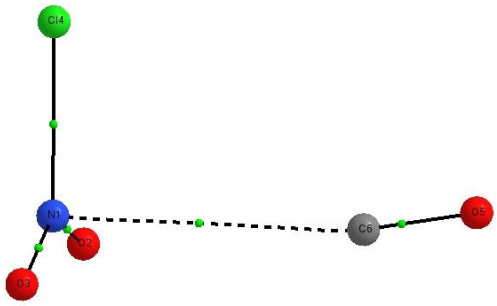
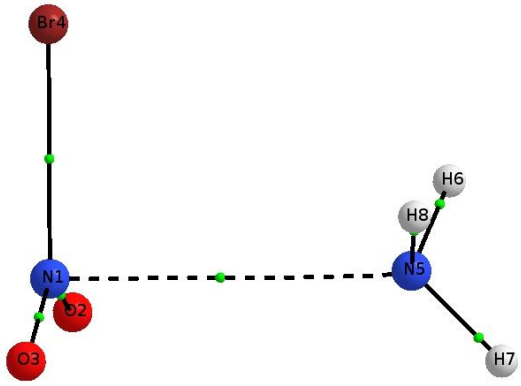
		
	NO_2-$CHCH_2$	NO_2-CCH

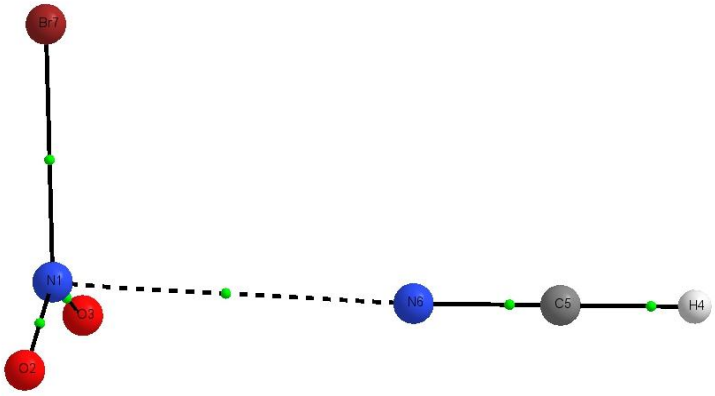
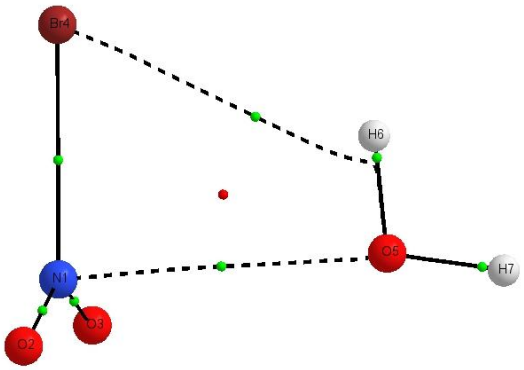
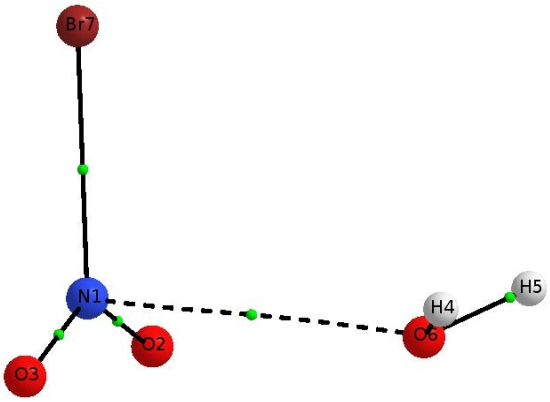
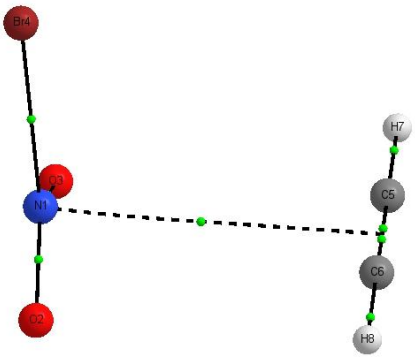
Fig. S2. Molecular graphs obtained with AIM theory for all the XNO_2 complexes.

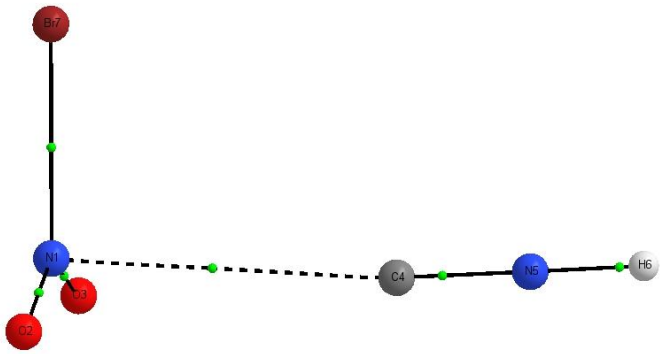
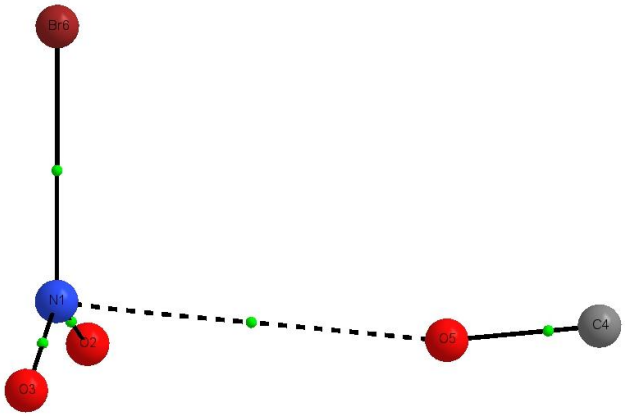
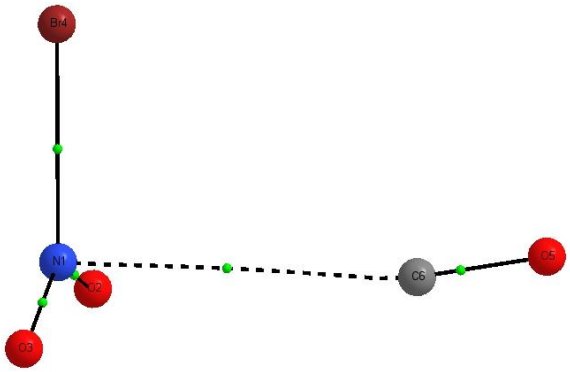
$H_3N\cdots NO_2F$	
$H_2O\cdots NO_2F$ (a)	
$HNC\cdots NO_2F$	
$HCN\cdots NO_2F$	
$HCCH\cdots NO_2F$ (per)[a]	

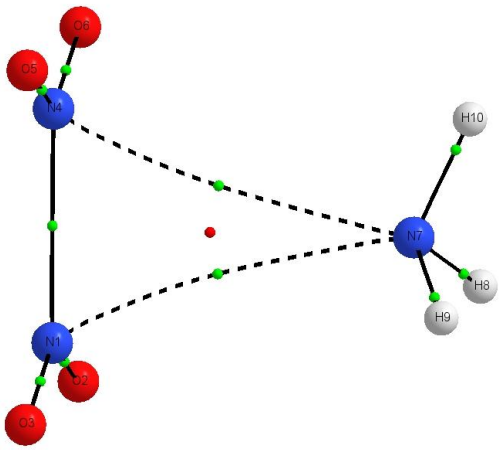
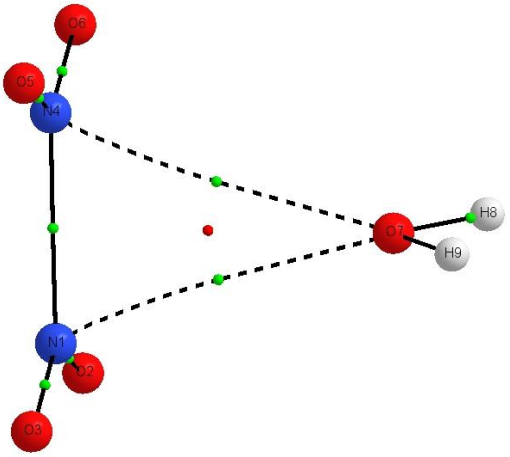
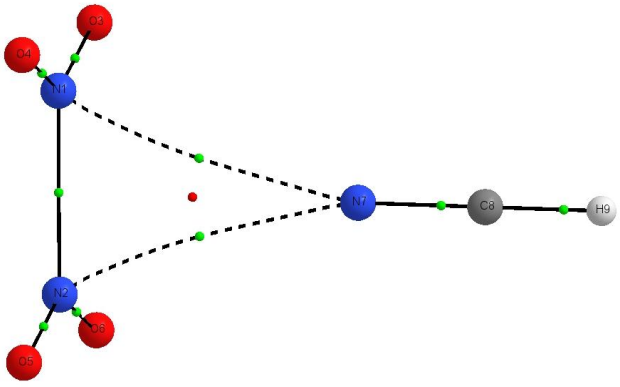
$HCCH\cdots NO_2F$ (par)[b]	
$CO\cdots NO_2F$	
$OC\cdots NO_2F$	
$H_3N\cdots NO_2Cl$	

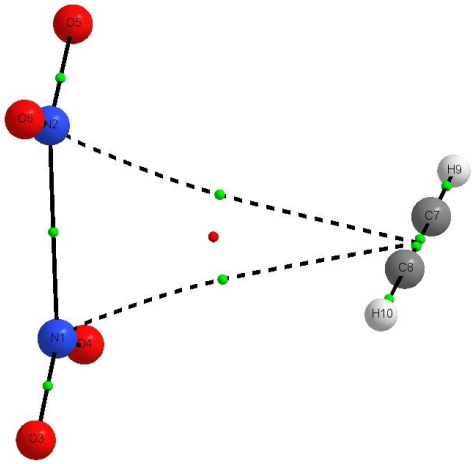
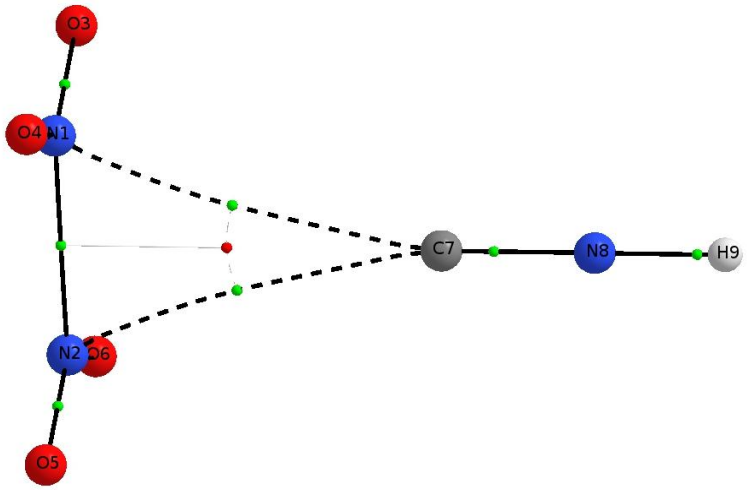
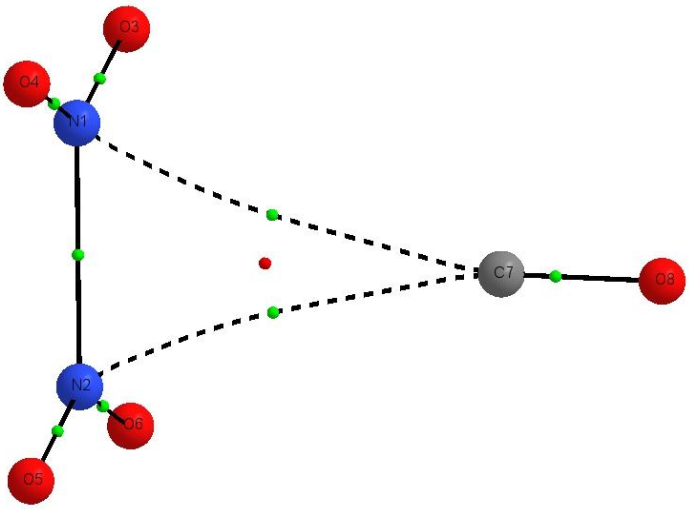
$H_2O\cdots NO_2Cl$ (a)	
$H_2O\cdots NO_2Cl$ (b)	
$HCN\cdots NO_2Cl$	
$HNC\cdots NO_2Cl$	

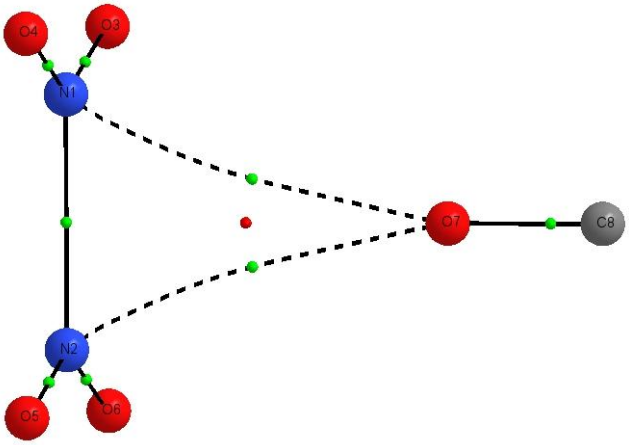
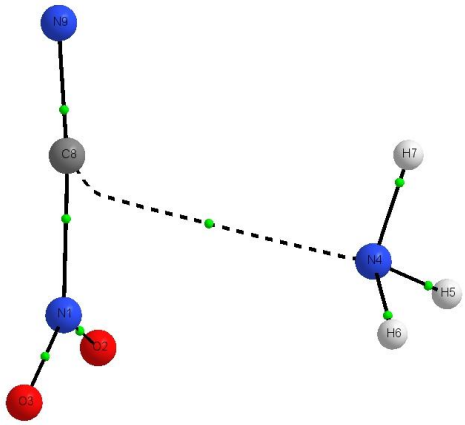
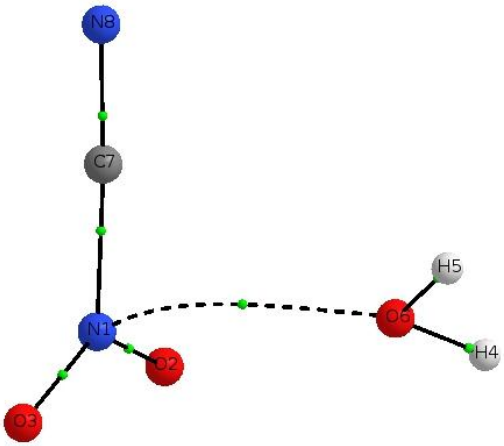
$HCCH\cdots NO_2Cl$[a]	
$CO\cdots NO_2Cl$	
$OC\cdots NO_2Cl$	
$H_3N\cdots NO_2Br$	

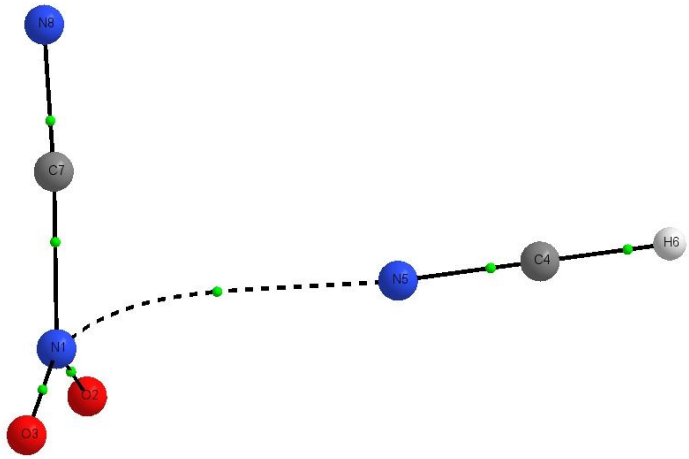
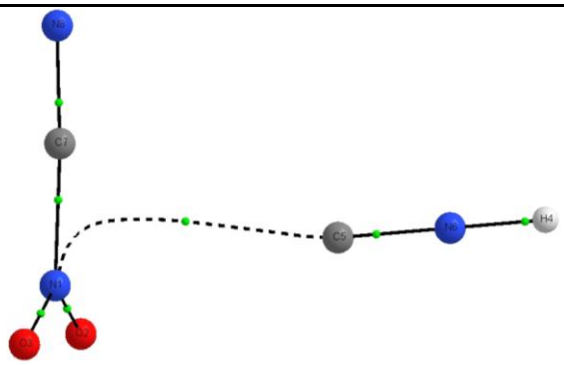
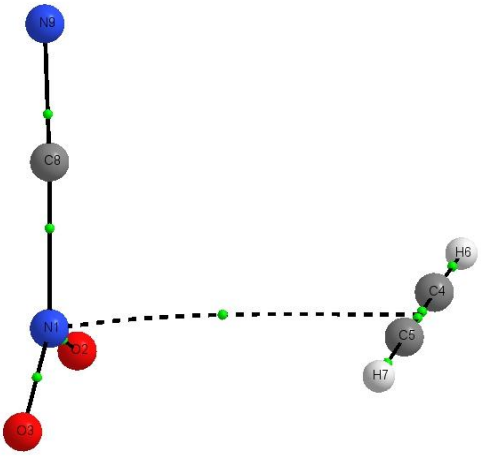
$HCN\cdots NO_2Br$	
$H_2O\cdots NO_2Br$(a)	
$H_2O\cdots NO_2Br$(b)	
$HCCH\cdots NO_2Br$[a]	

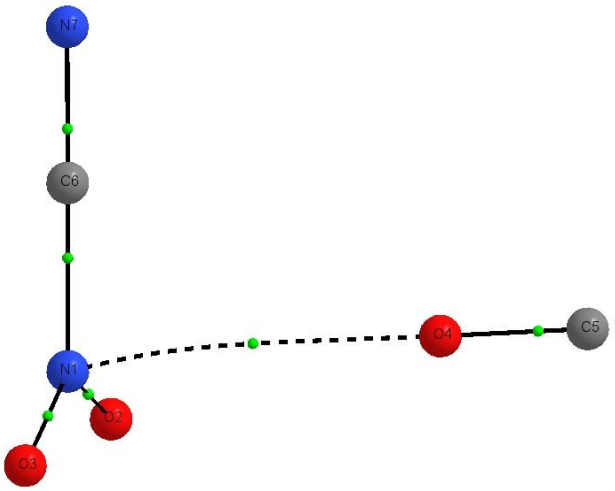
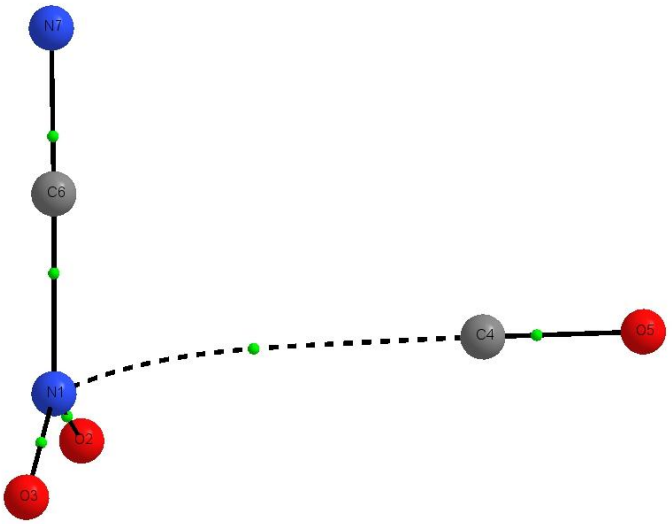
HNC···NO_2Br	
CO···NO_2Br	
OC···NO_2Br	

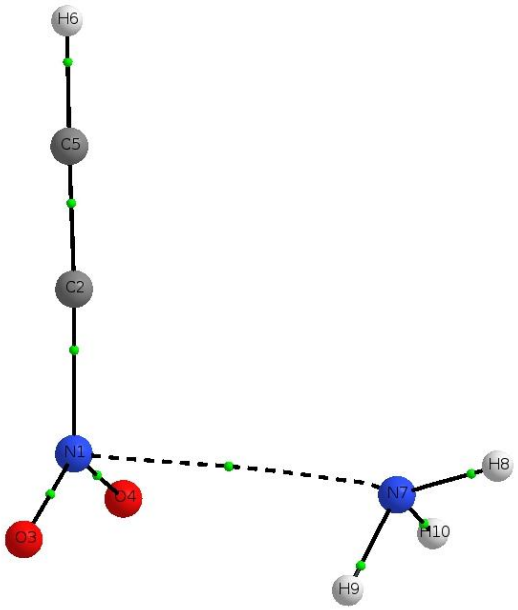
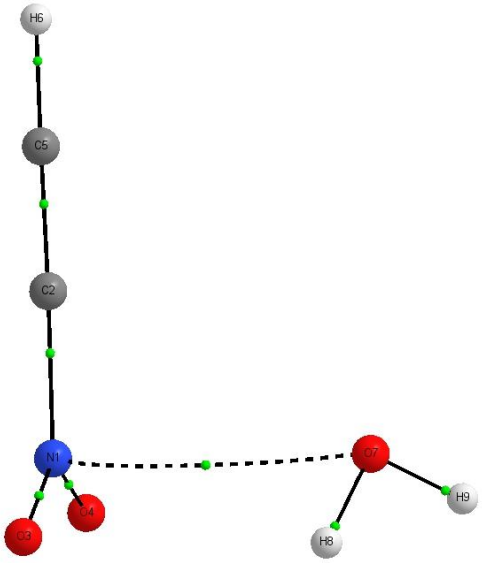
$H_3N\cdots NO_2\text{-}NO_2$	
$H_2O\cdots NO_2\text{-}NO_2$	
$HCN\cdots NO_2\text{-}NO_2$	

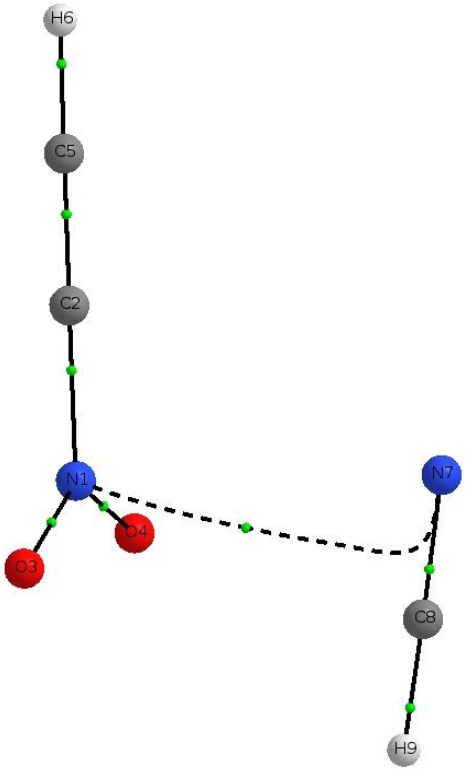
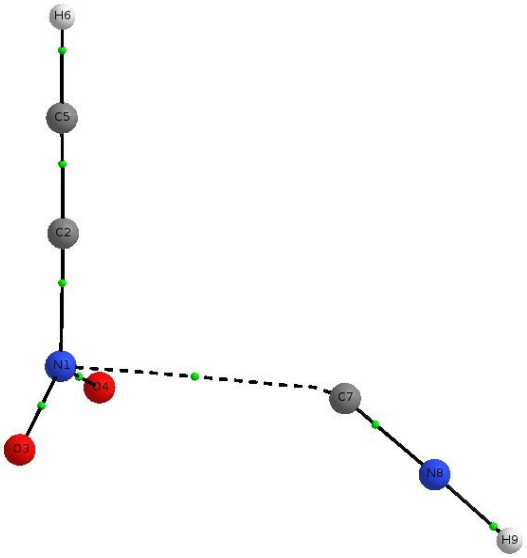
HCCH···NO_2-NO_2	
HNC···NO_2-NO_2	
CO···NO_2-NO_2	

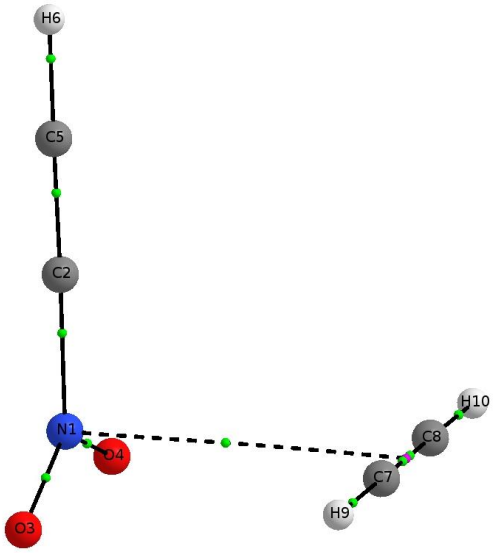
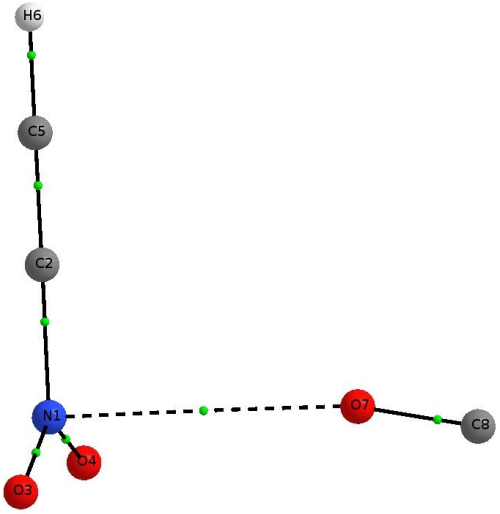
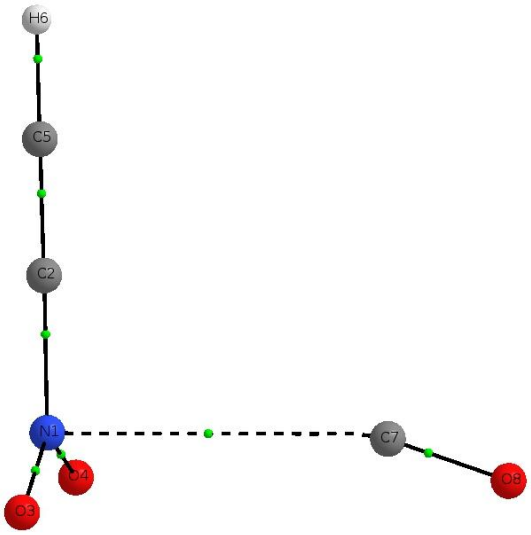
$OC\cdots NO_2\text{-}NO_2$	
$H_3N\cdots NO_2\text{-}CN$ (C··N)	
$H_2O\cdots NO_2\text{-}CN$	

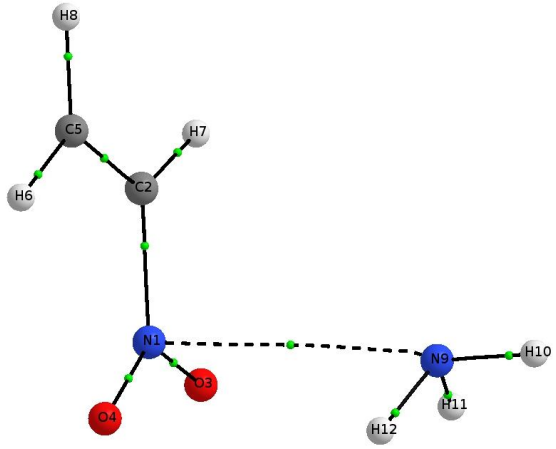
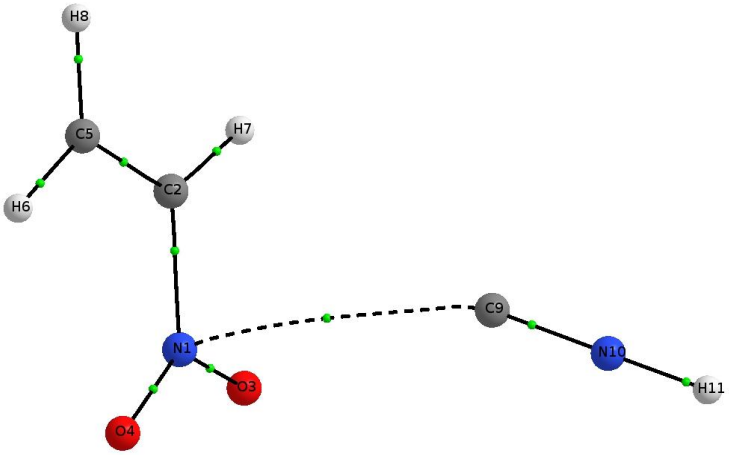
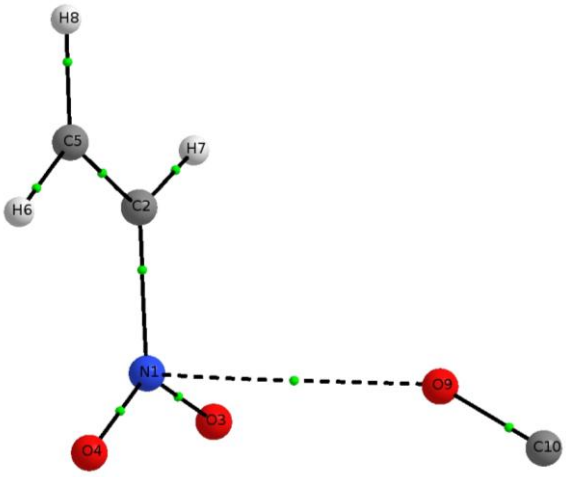
HCN···NO_2-CN	
HNC···NO_2-CN	
HCCH···NO_2-CN	

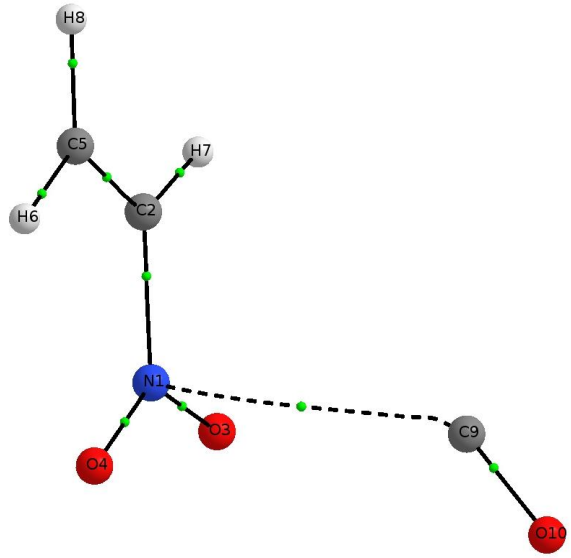
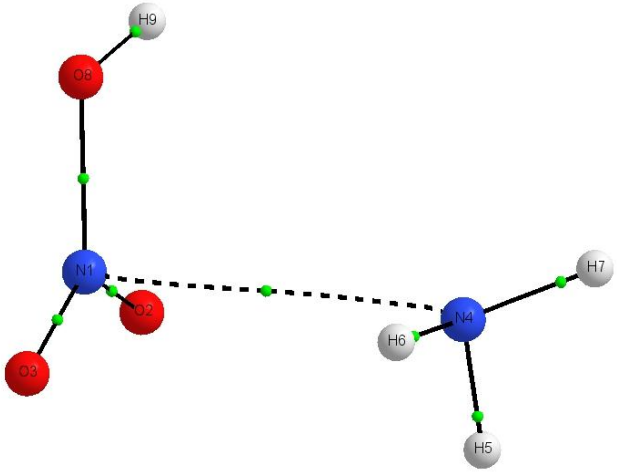
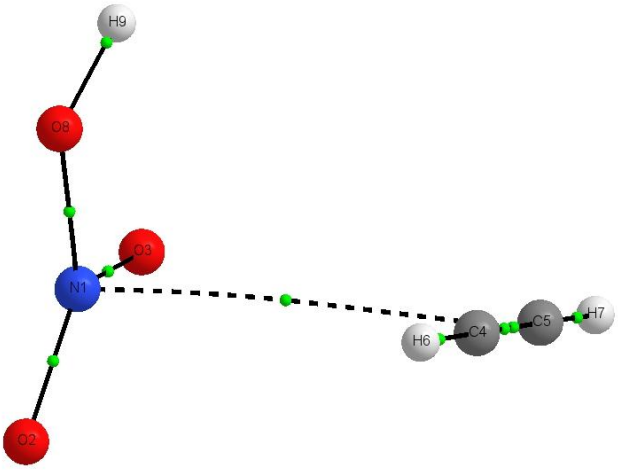
CO···NO_2-CN	
OC···NO_2-CN	

$H_3N\cdots NO_2$-CCH	
$H_2O\cdots NO_2$-CCH[b]	

HCN···NO_2-CCH	
HNC···NO_2-CCH	

HCCH···NO_2-CCH	
CO···NO_2-CCH	
OC···NO_2-CCH	

$H_3N\cdots NO_2\text{-}C_2H_3$	
$HNC\cdots NO_2\text{-}C_2H_3$	
$CO\cdots NO_2\text{-}C_2H_3$	

$OC\cdots NO_2\text{-}C_2H_3$	
$H_3N\cdots NO_2\text{-}OH$	
$HCCH\cdots NO_2\text{-}OH$	

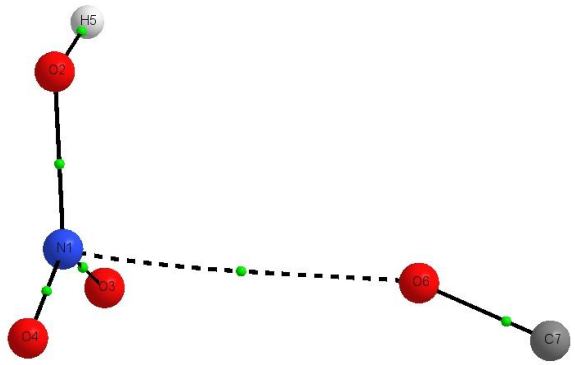
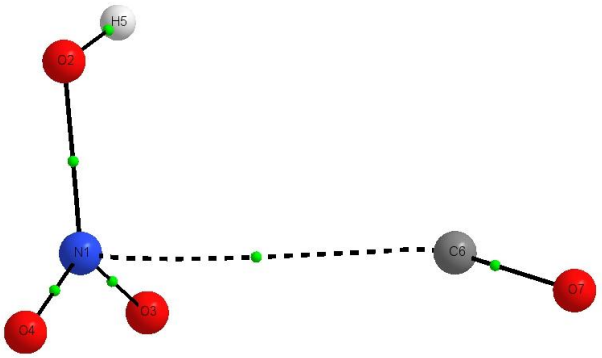
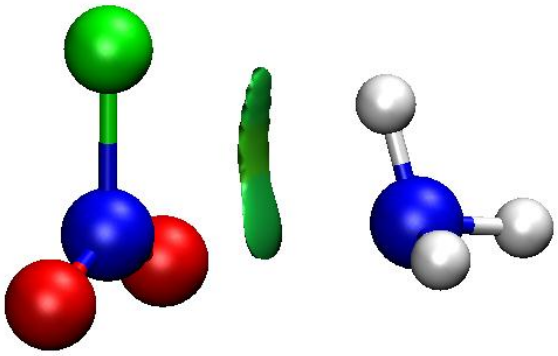
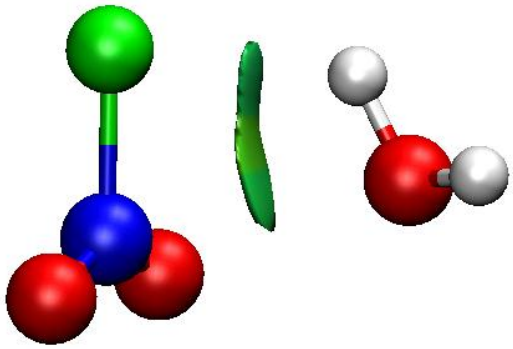
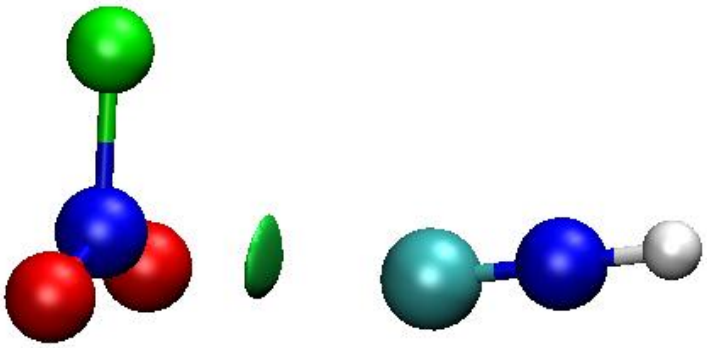
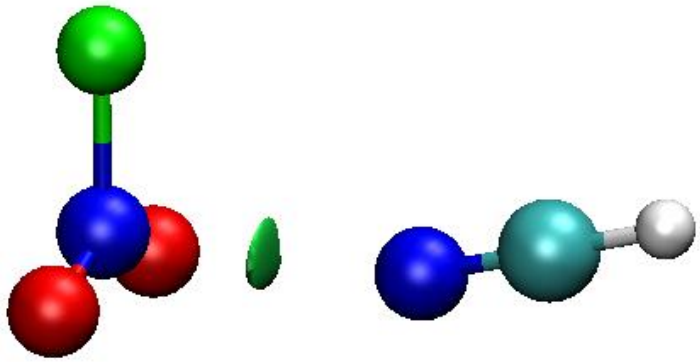
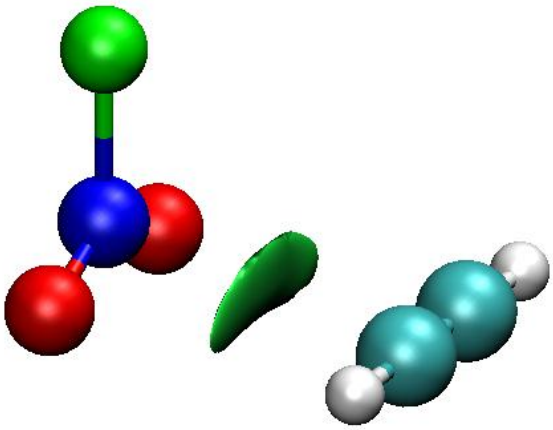
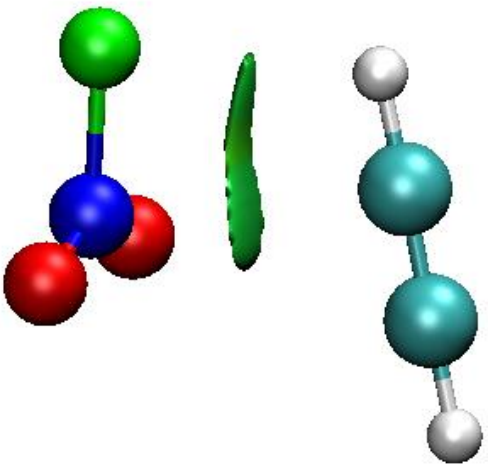
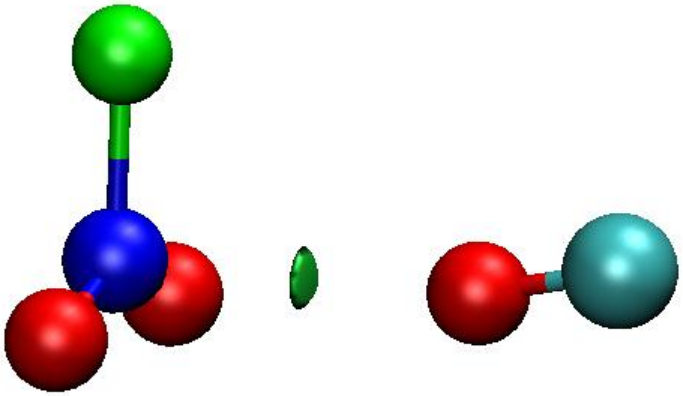
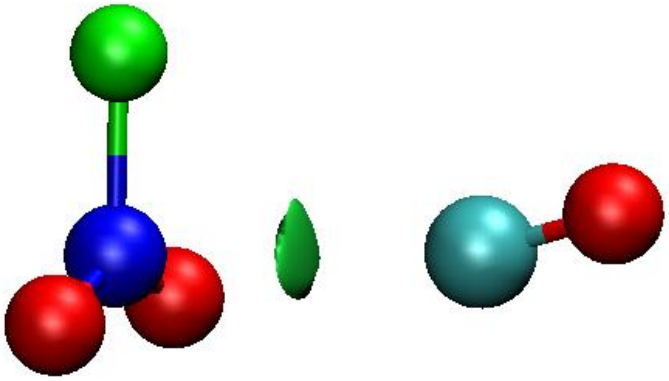
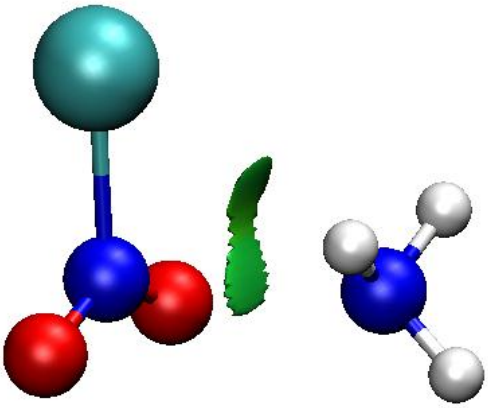
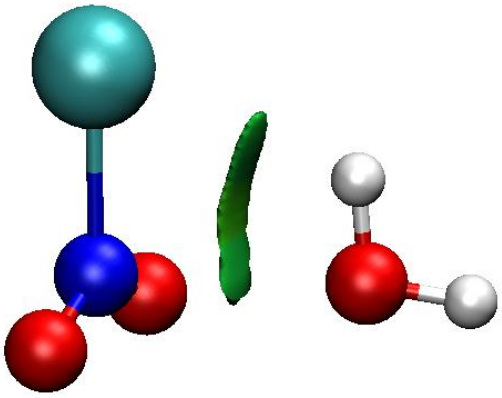
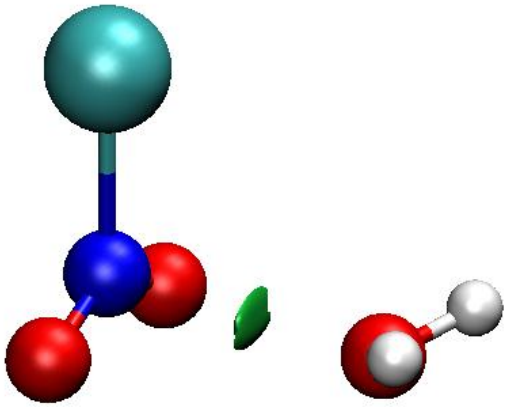
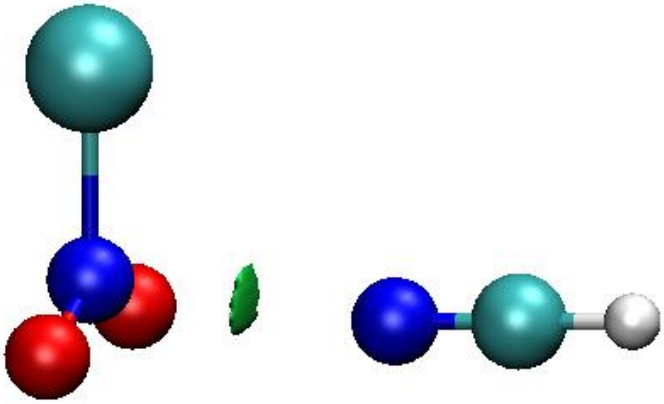
CO··· NO_2-OH	
OC··· NO_2-OH	

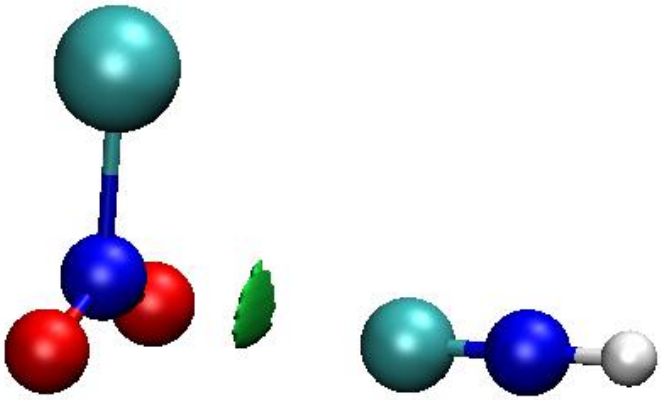
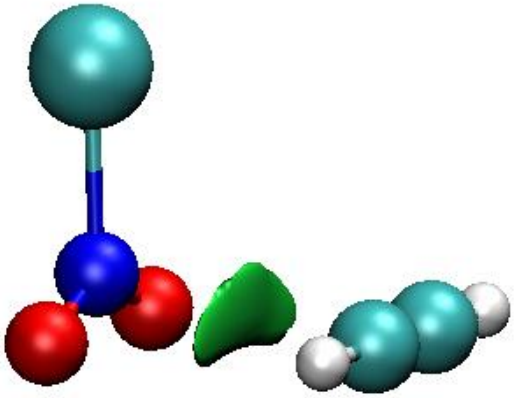
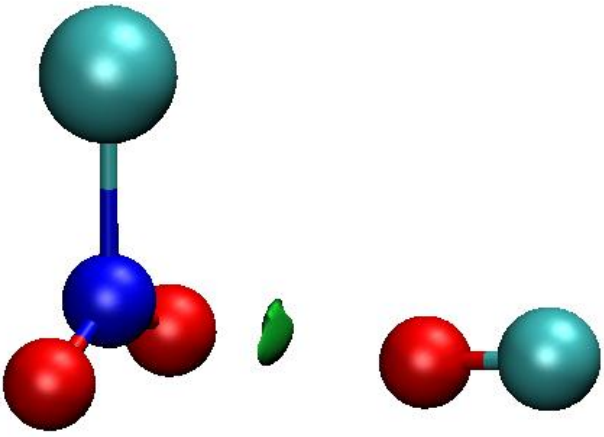
Fig. S3. NCI plot of the non-covalent interaction all the complexes. Blue areas are those with $\lambda 2 > 0$ (strong attractive), while green ones correspond to $\lambda 2 \approx 0$ (weak).. $\lambda 2$ is one of the three eigenvalues of the electron-density Hessian with $\lambda 1 \leq \lambda 2 \leq \lambda 3$.

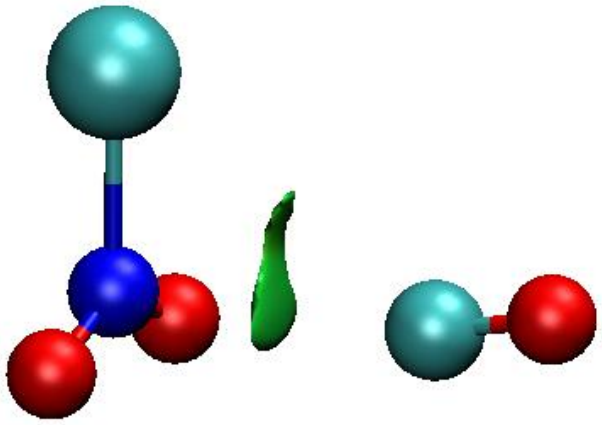
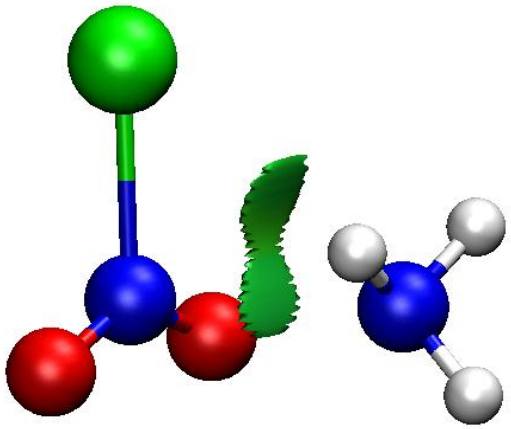
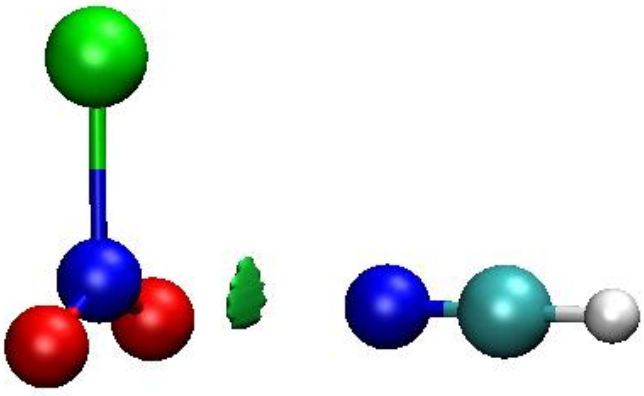
$H_3N\cdots NO_2F$	
$H_2O\cdots NO_2F$ (a)	
$HNC\cdots NO_2F$	

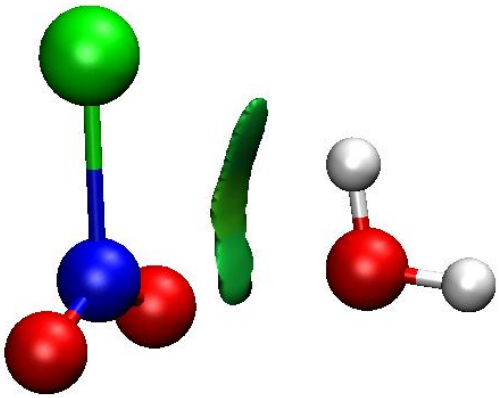
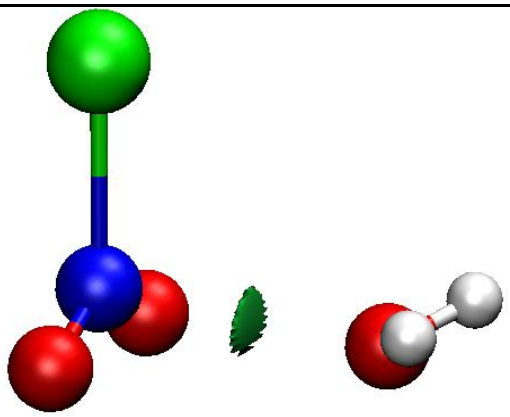
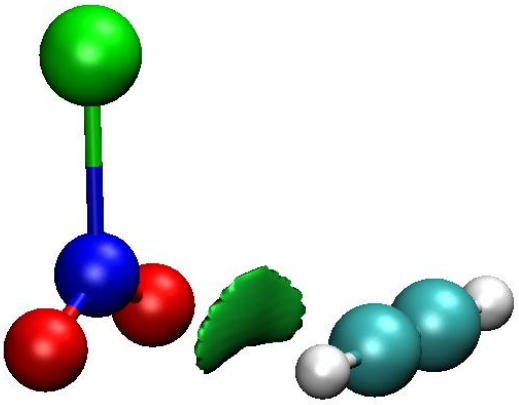
$HCN\cdots NO_2F$	
$HCCH\cdots NO_2F$ (per)[a]	
$HCCH\cdots NO_2F$ (par)[b]	

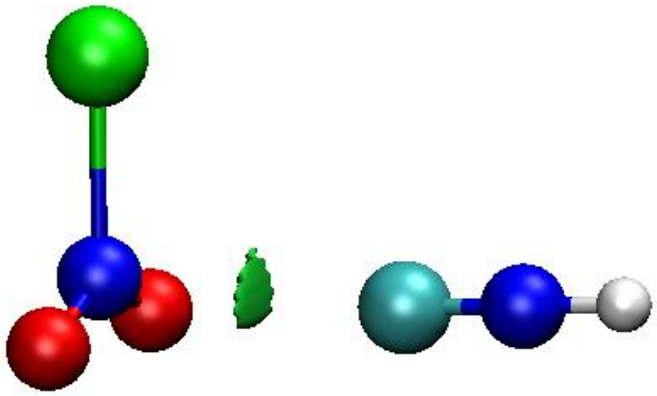
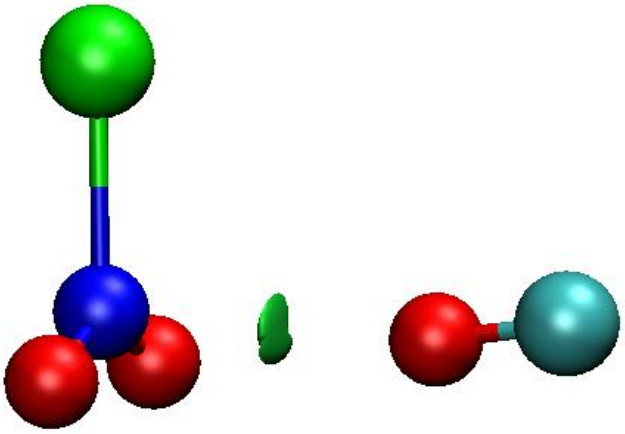
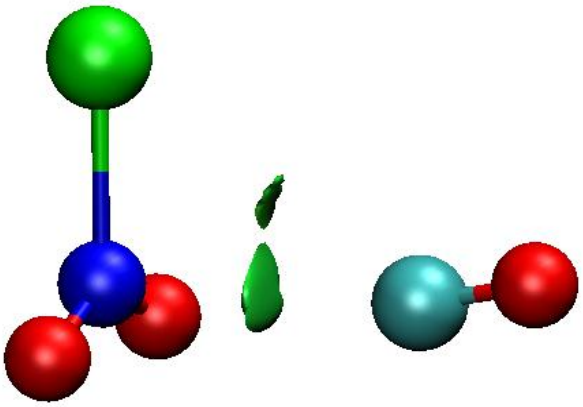
$CO\cdots NO_2F$	
$OC\cdots NO_2F$	
$H_3N\cdots NO_2Cl$	

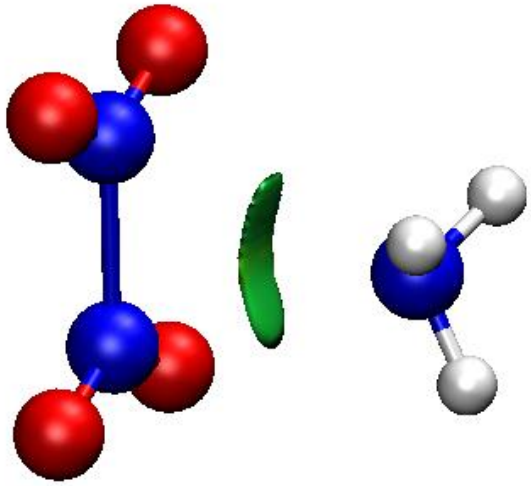
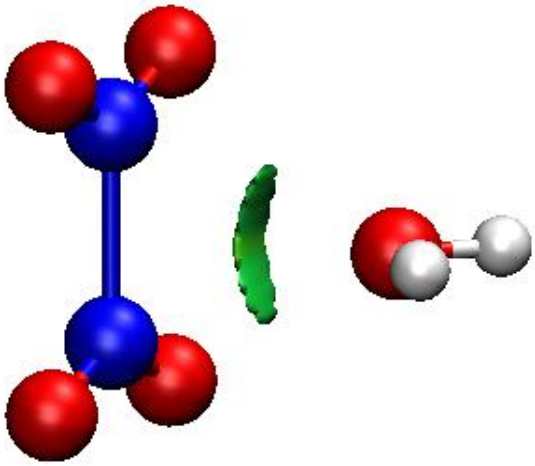
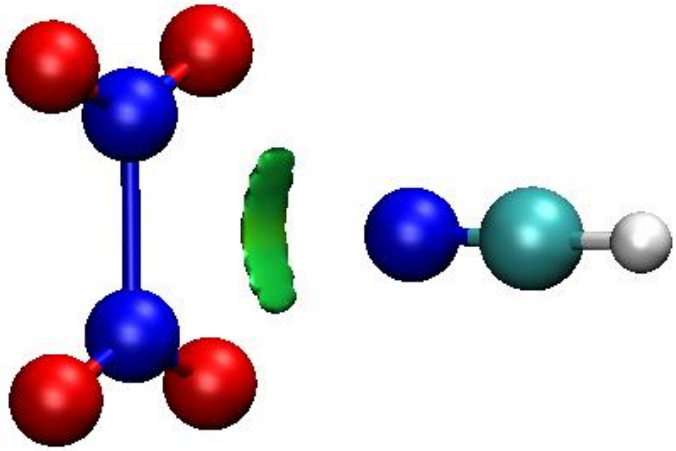
$H_2O\cdots NO_2Cl$ (a)	
$H_2O\cdots NO_2Cl$ (b)	
$HCN\cdots NO_2Cl$	

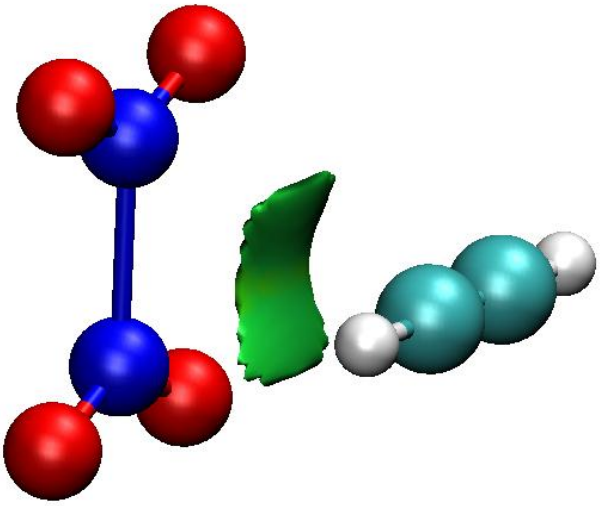
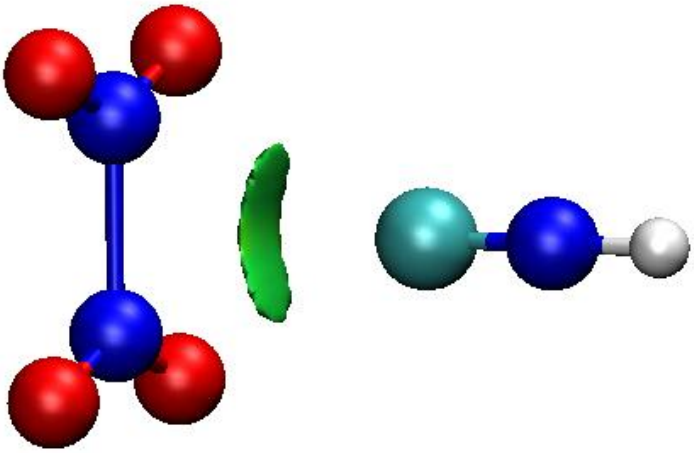
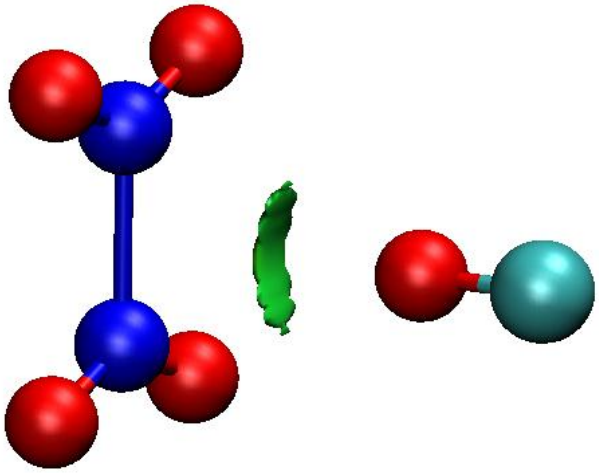
$HNC\cdots NO_2Cl$	
$HCCH\cdots NO_2Cl$[a]	
$CO\cdots NO_2Cl$	

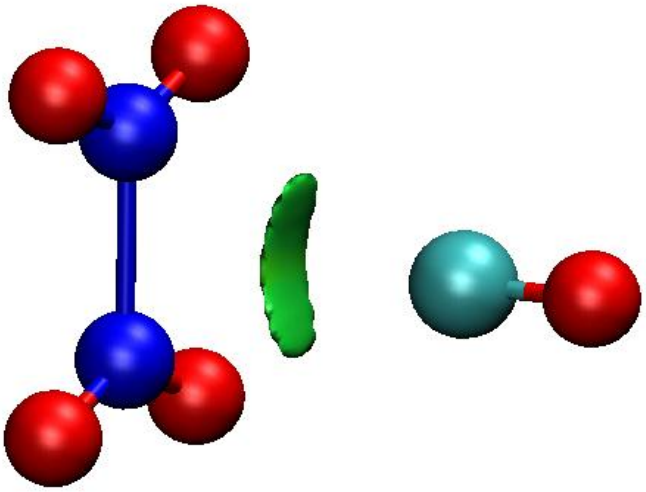
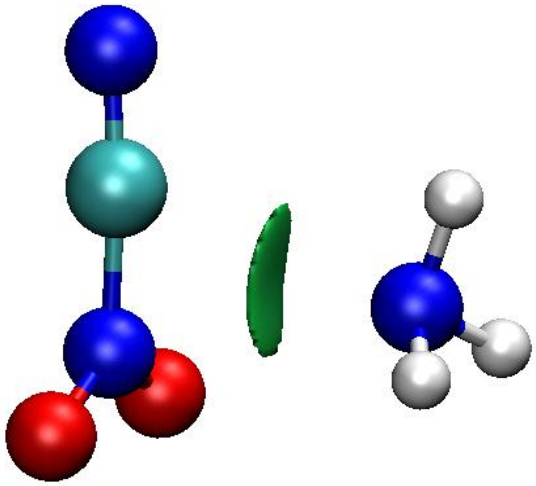
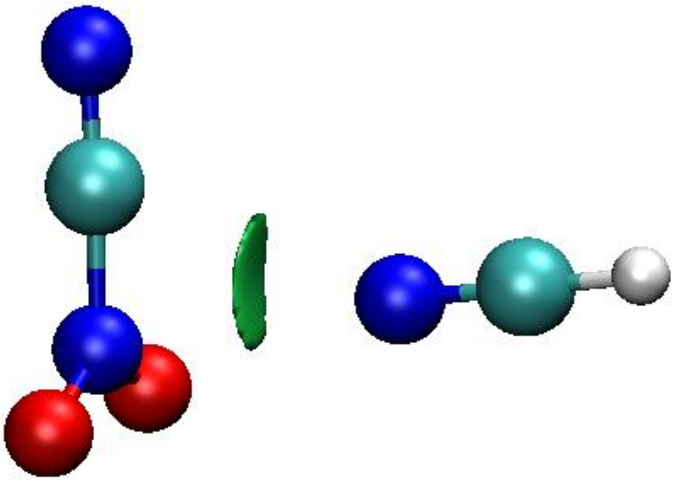
$OC\cdots NO_2Cl$	
$H_3N\cdots NO_2Br$	
$HCN\cdots NO_2Br$	

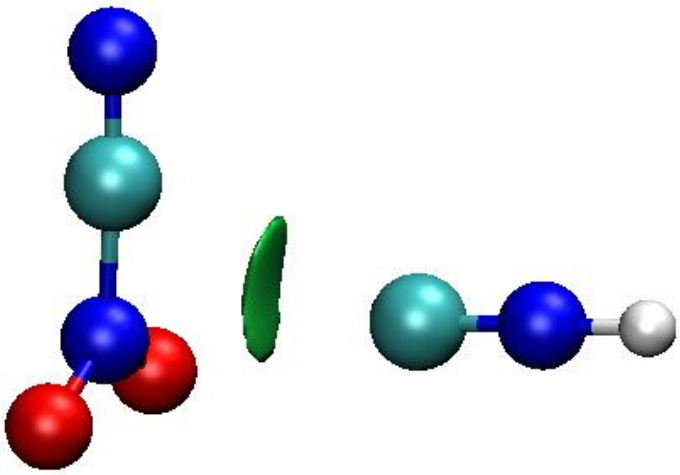
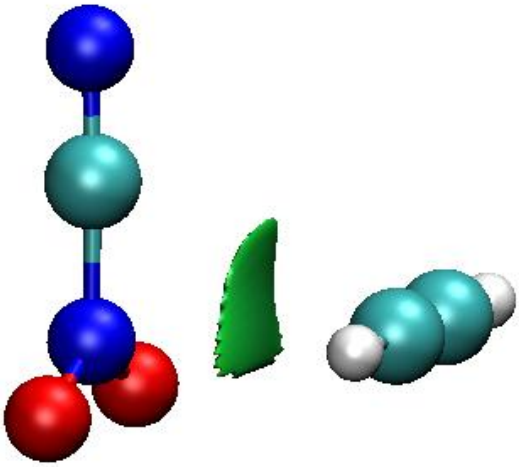
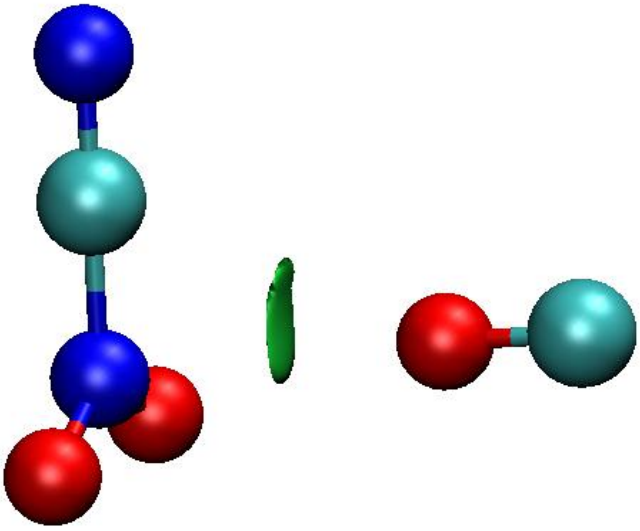
$H_2O\cdots NO_2Br$(a)	
$H_2O\cdots NO_2Br$(b)	
$HCCH\cdots NO_2Br$[a]	

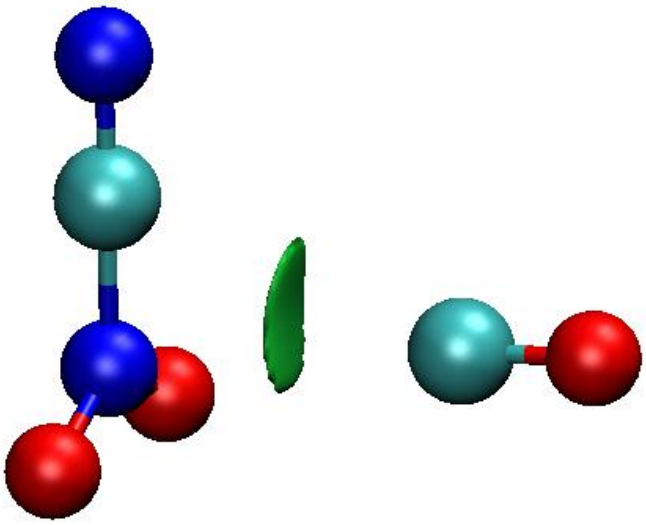
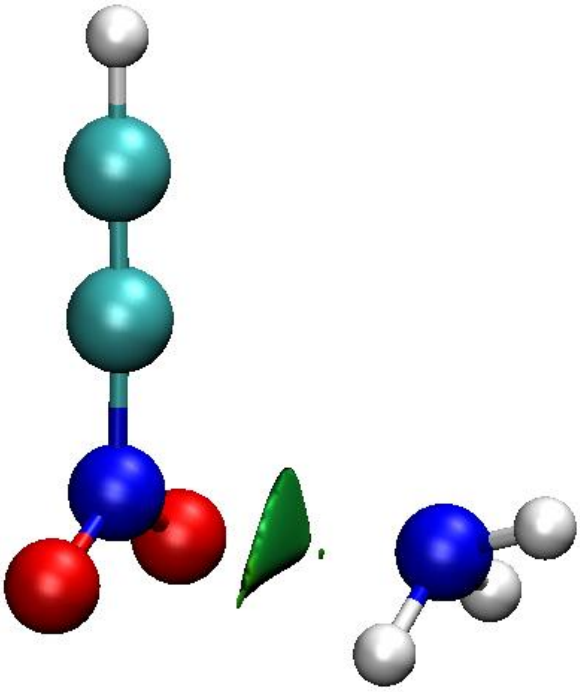
HNC···NO_2Br	
CO···NO_2Br	
OC···NO_2Br	

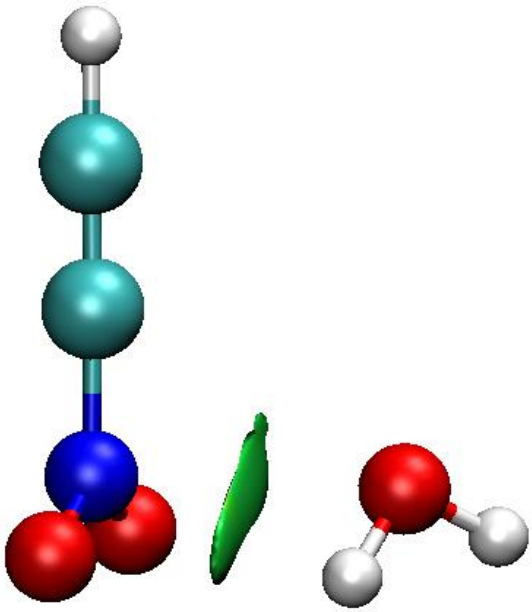
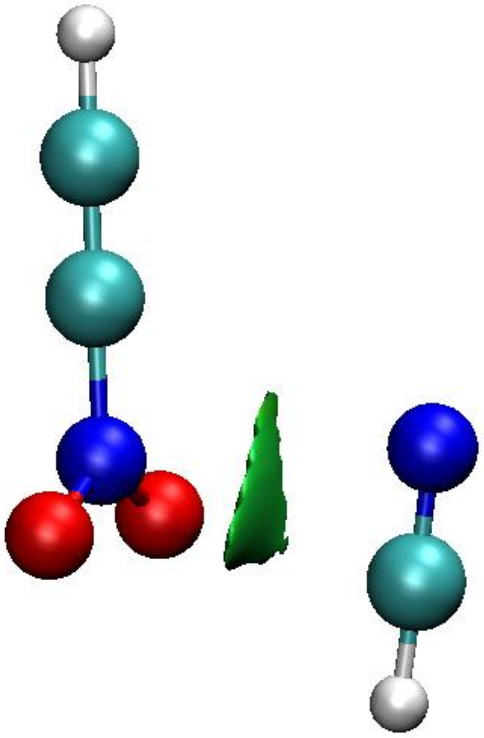
$H_3N\cdots NO_2\text{-}NO_2$	
$H_2O\cdots NO_2\text{-}NO_2$	
$HCN\cdots NO_2\text{-}NO_2$	

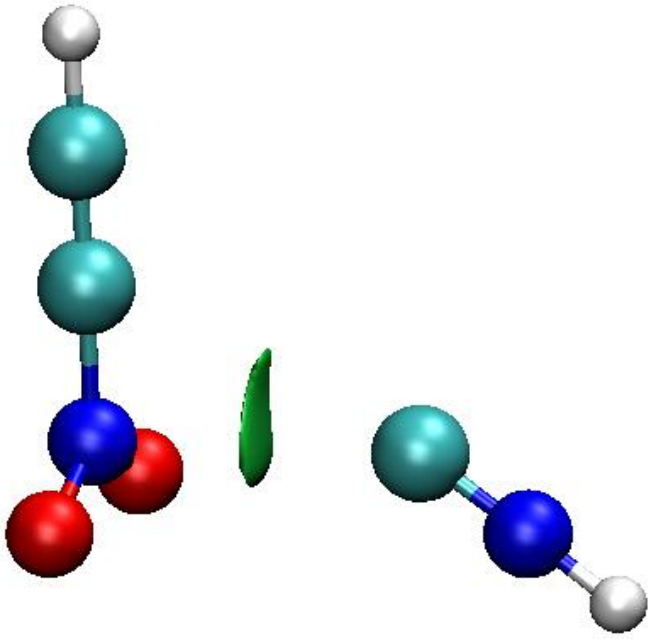
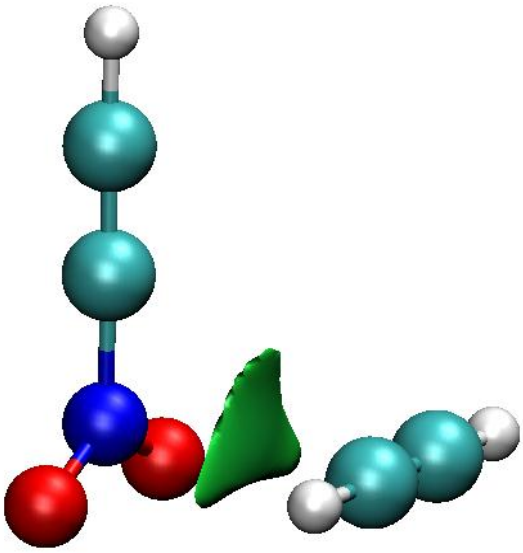
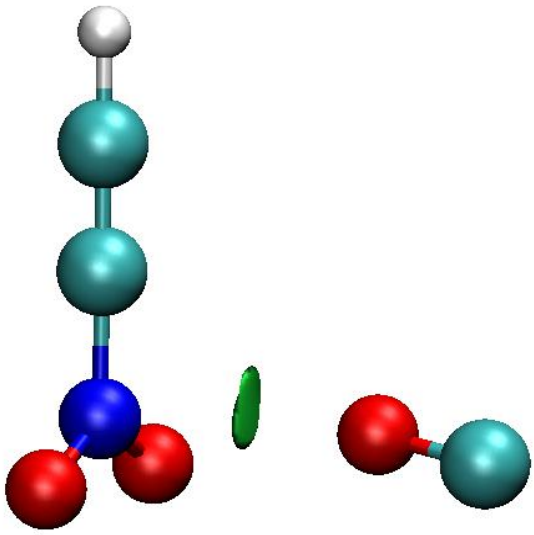
HCCH···NO_2-NO_2	
HNC···NO_2-NO_2	
CO···NO_2-NO_2	

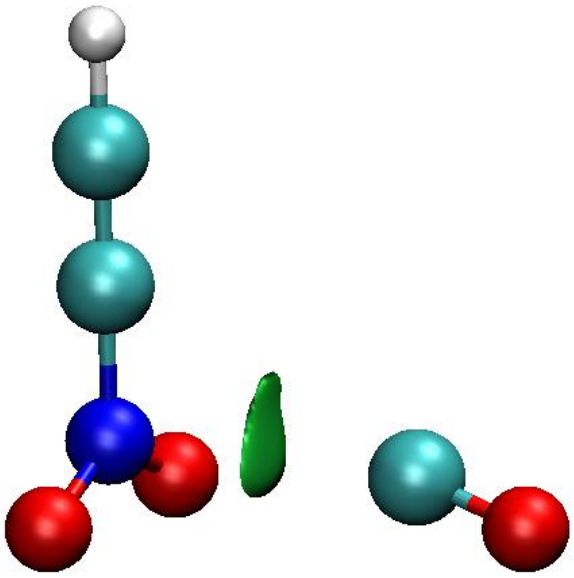
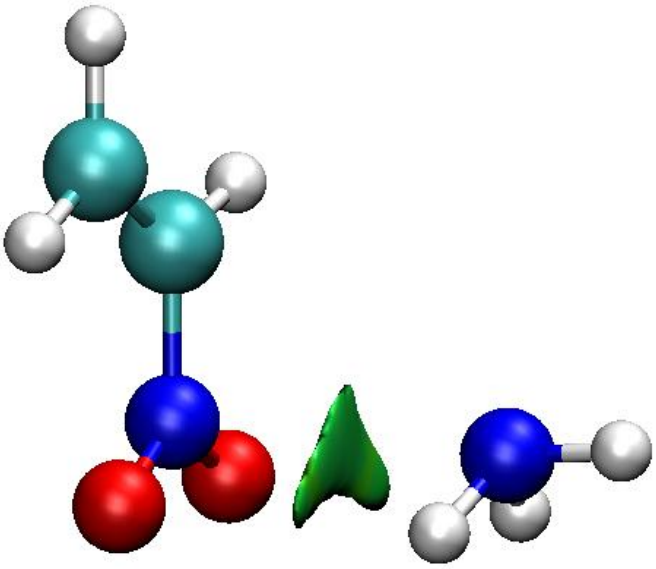
$OC\cdots NO_2\text{-}NO_2$	
$H_3N\cdots NO_2\text{-}CN$ (C··N)	
$HCN\cdots NO_2\text{-}CN$	

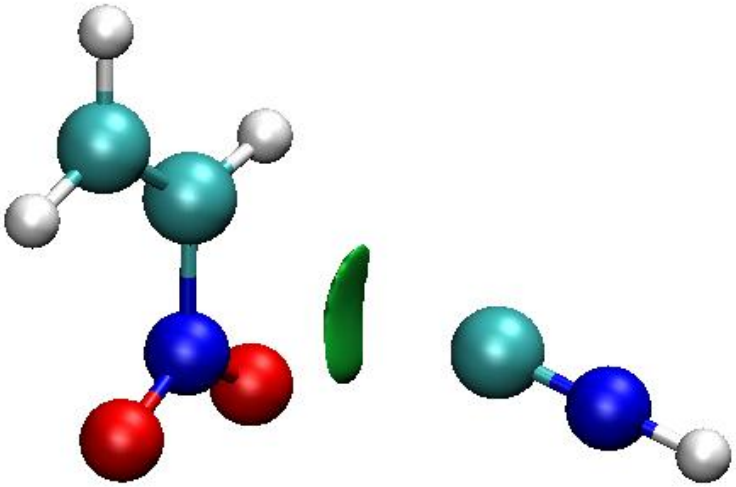
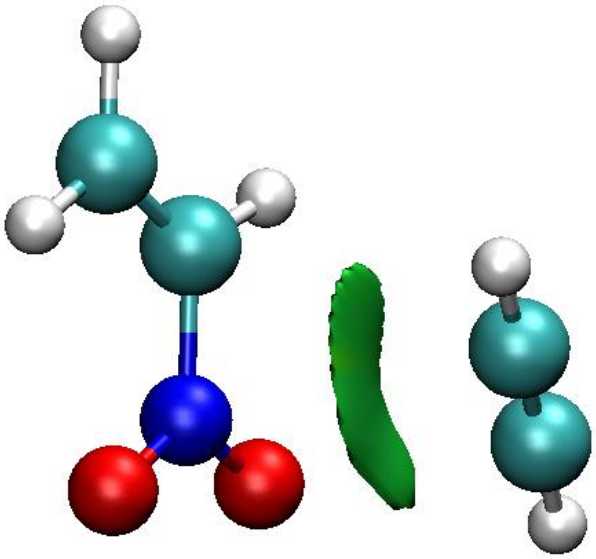
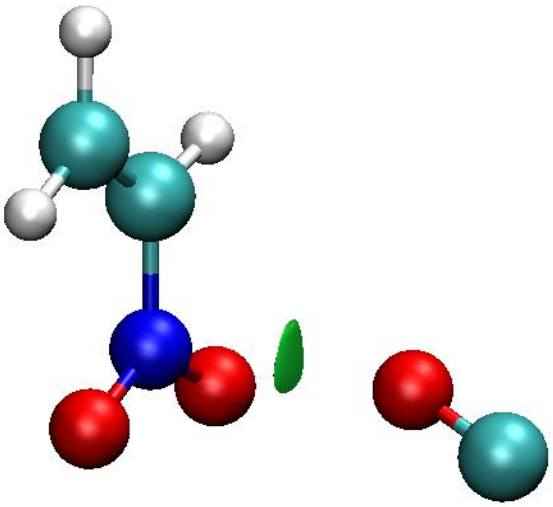
HNC···NO_2-CN	
HCCH···NO_2-CN	
CO···NO_2-CN	

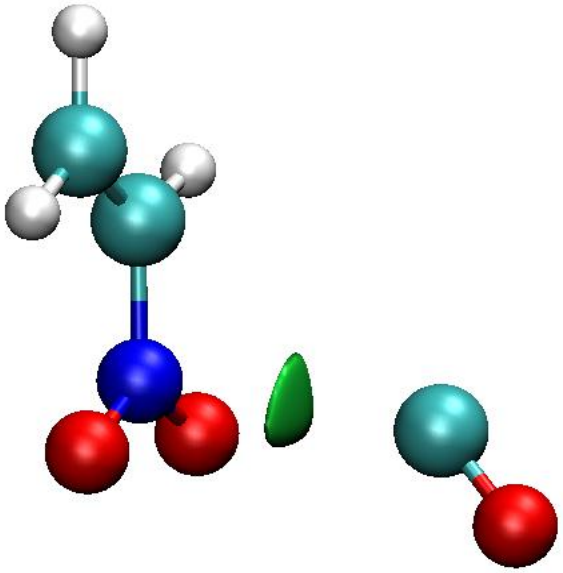
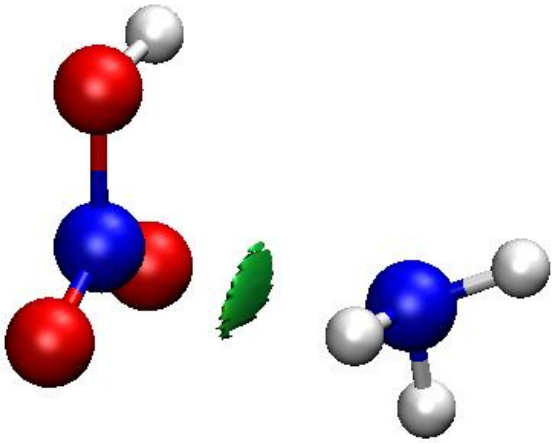
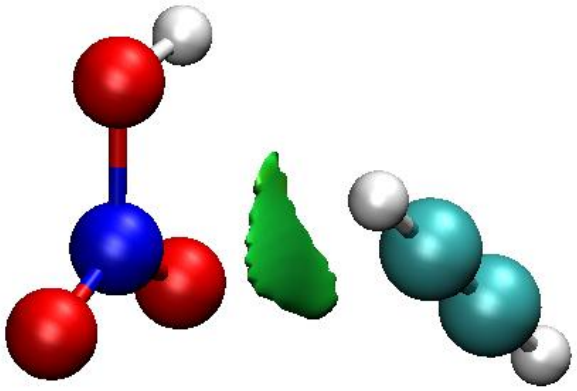
$OC\cdots NO_2\text{-}CN$	
$H_3N\cdots NO_2\text{-}CCH$	

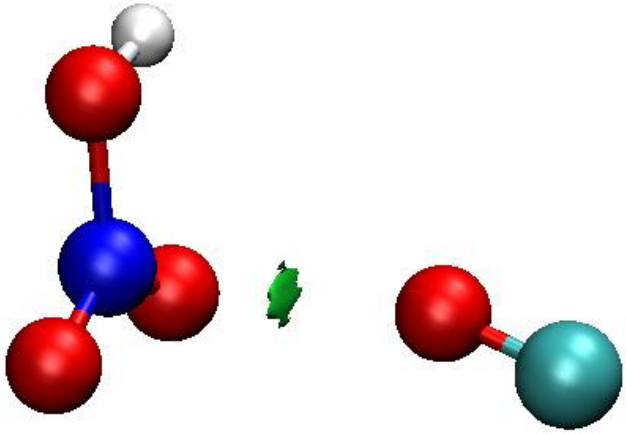
$H_2O\cdots NO_2$-CCH[b]	
HCN$\cdots NO_2$-CCH	

HNC···NO_2-CCH	
HCCH···NO_2-CCH	
CO···NO_2-CCH	

$OC\cdots NO_2\text{-}CCH$	
$H_3N\cdots NO_2\text{-}CHCH_2$	

HNC···NO_2-$CHCH_2$	
HCCH···NO_2-$CHCH_2$	
CO···NO_2-$CHCH_2$	

$OC\cdots NO_2\text{-}CHCH_2$	
$H_3N\cdots NO_2\text{-}OH$	
$HCCH\cdots NO_2\text{-}OH$	

CO⋯ NO_2-OH	
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