Supporting Information

Unrecognized Intramolecular and Intermolecular Attractive Interactions between Fluorine-Containing Motifs and Ether, Carbonyl and Amino Moieties

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Table S1. Atomic coordinates and energies obtained using MP2/aug-cc-pVTZ. They are minimum energy structures

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Me3N E = -174.101021

0 1
 N                  0.00000000    0.00000000    0.40685700
 C                  0.00000000    1.37311200   -0.06555900
 H                 -0.88441500    1.88970200    0.30552500
 H                  0.88441500    1.88970200    0.30552500
 H                  0.00000000    1.43149400   -1.16702800
 C                 -1.18915000   -0.68655600   -0.06555900
 H                 -1.19432200   -1.71077700    0.30552500
 H                 -2.07873800   -0.17892500    0.30552500
 H                 -1.23971100   -0.71574700   -1.16702800
 C                  1.18915000   -0.68655600   -0.06555900
 H                  2.07873800   -0.17892500    0.30552500
 H                  1.19432200   -1.71077700    0.30552500
 H                  1.23971100   -0.71574700   -1.16702800

acetone E = -192.611895

0 1
 C                  0.00000000    0.00000000    0.18307700
 O                  0.00000000    0.00000000    1.40380200
 C                  0.00000000    1.28668400   -0.61579500
 H                 -0.94451800    1.38293300   -1.16080900
 H                  0.11984800    2.13914500    0.05205400
 H                  0.80071800    1.27973200   -1.36091200
 C                  0.00000000   -1.28668400   -0.61579500
 H                 -0.80071800   -1.27973200   -1.36091200
 H                  0.94451800   -1.38293300   -1.16080900
 H                 -0.11984800   -2.13914500    0.05205400


dimethyl ether E= -154.737896

0 1
 O                  0.00000000    0.00000000    0.60193600
 C                  0.00000000    1.16178600   -0.19974900
 H                 -0.88882400    1.20025200   -0.83805500
 H                  0.00000000    2.01949800    0.46686200
 H                  0.88882400    1.20025200   -0.83805500
 C                  0.00000000   -1.16178600   -0.19974900
 H                  0.88882400   -1.20025200   -0.83805500
 H                  0.00000000   -2.01949800    0.46686200
 H                 -0.88882400   -1.20025200   -0.83805500
```

CF4 E = -436.999601

0 1

C	0.00000000	0.00000000	0.00000000
F	0.76271500	0.76271500	0.76271500
F	-0.76271500	-0.76271500	0.76271500
F	-0.76271500	0.76271500	-0.76271500
F	0.76271500	-0.76271500	-0.76271500

DME + CF4 E = -501.307720

0 1

C	-1.33255400	-0.00039700	0.00745800
F	-1.00597700	-1.07225900	-0.68966900
F	-0.99655400	1.09236800	-0.65133500
F	-0.71719900	-0.02345900	1.18014600
F	-2.64596800	0.00218200	0.21104600
O	1.77343400	-0.00031400	-0.47245200
C	2.29351000	1.16578500	0.13146600
H	3.38605700	1.21098300	0.03248600
H	1.85095500	2.01907700	-0.38160600
H	2.03290200	1.20860900	1.19756700
C	2.29730100	-1.16422800	0.13235400
H	2.03772700	-1.20666300	1.19872600
H	1.85672200	-2.01939000	-0.37941400
H	3.38989700	-1.20654500	0.03248300

acetone + CF4 E = -629.793109

0 1

C	-2.31675300	-0.06606500	-0.01668800
O	-1.27731000	-0.70307400	-0.07067600
C	-2.32433600	1.44205900	-0.00541700
H	-1.30674300	1.81999200	-0.00692800
H	-2.85857300	1.81171600	-0.88180000
H	-2.85856300	1.80633800	0.87275600
C	-3.66244300	-0.74391800	0.04207900
H	-4.16781400	-0.47512700	0.97072100
H	-4.29203300	-0.39611400	-0.77763300
H	-3.53999600	-1.82128400	-0.01277400
C	1.87489000	-0.02672500	0.00621900
F	1.57331400	-0.69243200	-1.08931300
F	1.51764200	-0.71637300	1.07027000
F	3.18550700	0.18080000	0.04245300
F	1.25843200	1.14433600	0.00369000

Me3N + CF4 E = -611.105877

0 1

N	0.00000000	0.00000000	-1.60326800
C	-0.00425300	-1.37525900	-2.06599100
H	0.87820800	-1.89139300	-1.68840500
H	-0.89088800	-1.88533800	-1.68996000
H	-0.00357100	-1.44499900	-3.16645200
C	1.19313600	0.68394600	-2.06599100
H	1.19889100	1.70624700	-1.68840500
H	2.07819500	0.17113800	-1.68996000
H	1.25319100	0.71940700	-3.16645200
C	-1.18888300	0.69131300	-2.06599100
H	-2.07709800	0.18514600	-1.68840500
H	-1.18730700	1.71420100	-1.68996000
H	-1.24962000	0.72559200	-3.16645200
C	0.00000000	0.00000000	1.60993600
F	0.00000000	1.24876700	1.18320000
F	0.00000000	0.00000000	2.93768400
F	1.08146400	-0.62438400	1.18320000
F	-1.08146400	-0.62438400	1.18320000

Me3P = -460.358012

0 1

P	0.00000000	0.00000000	0.61120100
C	0.00000000	1.61560100	-0.28239700
H	-0.88192600	2.18939100	0.00156700
H	0.88192600	2.18939100	0.00156700
H	0.00000000	1.47120900	-1.36475800
C	-1.39915200	-0.80780100	-0.28239700
H	-1.45510500	-1.85846500	0.00156700
H	-2.33703100	-0.33092500	0.00156700
H	-1.27410400	-0.73560500	-1.36475800
C	1.39915200	-0.80780100	-0.28239700
H	2.33703100	-0.33092500	0.00156700
H	1.45510500	-1.85846500	0.00156700
H	1.27410400	-0.73560500	-1.36475800

Me3P-CF4 E = -897.360050

1

P	1.72978100	0.00198100	-0.14644800
C	-2.30316500	0.00176400	-0.05087100
F	-2.00901300	-1.17908500	-0.56143200
F	-3.61786900	0.10557800	0.07866100
F	-1.74081000	0.12379300	1.13869200
F	-1.86801000	0.95589200	-0.84976600
C	3.01117400	-0.85197400	-1.16473000
H	3.06307100	-0.38347500	-2.14708300
H	3.99319000	-0.79744500	-0.68996800
H	2.73691900	-1.89735100	-1.30115100
C	2.60512100	1.60951200	0.09472500

H	2.66685700	2.13382500	-0.85851600
H	2.04576500	2.23406500	0.79019900
H	3.61385700	1.45356800	0.48304900
C	2.10854300	-0.76786200	1.48777600
H	1.55006300	-0.25407900	2.26989000
H	1.79922400	-1.81256700	1.48099900
H	3.17562800	-0.71049400	1.71248800

AX-OCH3 THP E(MP2/6-311+G*) =-385.216376

0 1

C	-1.57355900	-0.87317500	-0.59378800
C	-0.61627300	-1.37757500	0.48643700
C	0.55978800	-0.42892400	0.65294000
C	-0.71046800	1.42052800	-0.11695300
C	-1.96283900	0.57395600	-0.28774900
H	1.16929800	-0.68849200	1.53007300
H	-1.13567300	-1.43346200	1.45017900
H	-0.23261300	-2.37584600	0.25443200
H	-1.08355600	-0.92711100	-1.57191600
H	-2.46195400	-1.51198400	-0.63937000
H	-0.94673100	2.43727800	0.20424100
H	-0.15572100	1.47519600	-1.06309900
H	-2.55032900	0.61688800	0.63753300
H	-2.58124000	0.99634600	-1.08878800
O	0.14233900	0.89917100	0.91023300
O	1.34073500	-0.52004600	-0.51494500
C	2.55319800	0.21635000	-0.41811500
H	2.36295800	1.28677100	-0.29950200
H	3.09902500	0.03837600	-1.34411800
H	3.15286500	-0.13391900	0.43139500

AX-OCF3 THP E(MP2/6-311+G*) = -682.515248

0 1

C	-2.33737600	0.85082400	0.74933500
C	-1.53046500	1.42416700	-0.41500500
C	-0.38386900	0.50310000	-0.79123600
C	-1.50476500	-1.40127500	0.07246900
C	-2.74056400	-0.58658300	0.41732800
H	0.12110800	0.82289900	-1.70407000
H	-2.16667600	1.51637400	-1.30282200
H	-1.12851300	2.41615000	-0.18966400
H	-1.73304400	0.86741600	1.66302100
H	-3.21996300	1.47106800	0.93463200
H	-1.75673700	-2.40187700	-0.28202500
H	-0.84629200	-1.49953000	0.94321500

H	-3.42924600	-0.59697300	-0.43597100
H	-3.25753000	-1.05835900	1.26078400
O	-0.76454500	-0.81337800	-1.01351900
O	0.56073200	0.61560300	0.31375300
C	1.75946300	0.02531400	0.16701200
F	1.72068400	-1.30490600	0.35700200
F	2.30065800	0.23015300	-1.04762000
F	2.58675300	0.53605700	1.08079700

Table S2 Summary of complex energies, HF and MP2 calculations

CF4,HF	-435.770692	CF4 HF big	-435.823661		CF4,MP2	-436.724099	CF4, MP2big	-436.999601
DME.HF	-154.103886	DME HF big	-154.129764		DME, MP2	-154.578755	DME,MP2big	-154.737896
sum	-589.874578	sum	-589.953425		sum	-591.302854	sum	-591.737497
pair	-589.876611	pair	-589.954392		pair	-591.30792	pair	-591.741947
difference	1.28	difference	0.61		difference	3.18	difference	2.79

Me2COHF	-192.007995	Me2CO HF big	-192.037751		Me2COmp2	-192.61189	Me2CObig	-192.790143
sum	-627.778687	sum	-627.861412		sum	-629.335989	sum	-629.789744
pair	-627.780505	pair	-627.862467		pair	-629.340194	pair	-629.793109
difference	1.14	difference	0.66		difference	2.64	difference	2.11

Me3NHF	-173.306112	Me3NHF big	-173.336039		Me3Nmp2	-173.901911	Me3Nbig	-174.101021
	-609.076804		-609.159700		sum	-610.626010	sum	-611.100622
	-609.078923		-609.160676		pair	-610.632070	pair	-611.105877
	1.33		0.61		difference	3.80	difference	3.30

big=aug-cc-pVTZ
small=6-311G*

Table S3 Hirshfeld charges for reactants and complexes

MP2/aug-cc-pVTZ Hirshfeld charges for Me3N-CF4			
atom	reactants	complex	change
N1	-0.1042	-0.0987	0.0055
C2	-0.0456	-0.0466	-0.0010
H3	0.0328	0.0313	-0.0015
H4	0.0328	0.0313	-0.0015
H5	0.0148	0.0157	0.0009
C6	-0.0456	-0.0466	-0.0010
H7	0.0328	0.0313	-0.0015
H8	0.0328	0.0313	-0.0015
H9	0.0148	0.0157	0.0009
C10	-0.0456	-0.0466	-0.0010
H11	0.0328	0.0313	-0.0015
H12	0.0328	0.0313	-0.0015
H13	0.0148	0.0157	0.0009
C14	0.3721	0.3716	-0.0005
F15	-0.0930	-0.0877	0.0053
F16	-0.0930	-0.1046	-0.0116
F17	-0.0930	-0.0877	0.0053
F18	-0.0930	-0.0877	0.0053
sum all	0.0002	0.0004	
sum CF4	0.0001	0.0039	
sum Me3N	0.0001	-0.0035	
Me2	0.0347	0.0317	-0.0030
Me6	0.0347	0.0317	-0.0030
Me10	0.0347	0.0317	-0.0030

MP2/aug-cc-pVTZ Hirshfeld charges for DME-CF4

atom	reactant	complex	change
C1	0.3721	0.3737	0.0016
F2	-0.0930	-0.0853	0.0077
F3	-0.0930	-0.0853	0.0077
F4	-0.0930	-0.0850	0.0080
F5	-0.0930	-0.1008	-0.0078
O6	-0.1733	-0.1716	0.0017
C7	-0.0069	-0.0108	-0.0039
H8	0.0264	0.0272	0.0008
H9	0.0407	0.0383	-0.0024
H10	0.0264	0.0224	-0.0040
C11	-0.0069	-0.0108	-0.0039
H12	0.0264	0.0272	0.0008
H13	0.0407	0.0383	-0.0024
H14	0.0264	0.0224	-0.0040
sum all	0.0000	-0.0001	
sum CF4	0.0001	0.0173	
sum DME	-0.0001	-0.0174	
Me7	0.0866	0.0771	-0.0095
Me11	0.0866	0.0771	-0.0095

Me2CO-CF4 Hirshfeld charges from MP2/aug-cc-pVTZ calcuations

atom	reactants	complex	change
C1	0.1649	0.1666	0.0017
O2	-0.2443	-0.2368	0.0075
C3	-0.0920	-0.0929	-0.0009
H4	0.0441	0.0381	-0.0060
H5	0.0436	0.0449	0.0013
H6	0.0441	0.0440	-0.0001
C7	-0.0920	-0.0916	0.0004
H8	0.0441	0.0450	0.0010
H9	0.0436	0.0442	0.0006
H10	0.0441	0.0439	-0.0001
C11	0.3721	0.3705	-0.0016
F12	-0.0930	-0.0895	0.0035
F13	-0.0930	-0.0900	0.0030
F14	-0.0930	-0.1045	-0.0115
F15	-0.0930	-0.0919	0.0011
sum all	0.0001	0.0001	
sum CF4	0.0001	-0.0054	
sum Me2C	0.0000	0.0055	
Me3	0.0397	0.0341	-0.0056
Me7	0.0397	0.0416	0.0019