Electronic Supplementary Information for

Computational evidence that hyperconjugative orbital interactions are responsible for the stability of intramolecular Te…O/Te…S non-covalent interactions and comparable to hydrogen bonds in quasi-cyclic systems

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Table S1 Calculated energies (KJ/mol) of Te…O, Te…S, N-H…O and N-H…S in water at M06-2X/aug-cc-pVQZ method

Types of Interactions	Interaction Energies (kJ/mol)
Te…O	20.8
Te…S	25.6
N-H…O*	16.8
N-H…S*	15.5

*Systems are taken from the reference-21 (3(Z)/3(E), 4(Z)/4(E) compounds in ref. 21) and optimized at M06-2X/aug-cc-pVQZ level of theory.

Table S2 Calculated relative energies (KJ/mol) of E/Z isomers of 3(Z)-6(E) in gas phase at M06-2X/aug-cc-pVQZ method.

Molecules	Energy	ΔE
3F(Z)	-299.23376410	0.0
3F(E)	-299.19591217	99.5
4CH3(Z)	-239.24771591	0.0
4CH3(E)	-239.23775792	26.0

5F(Z)	-622.20023849	0.0
5F(E)	-622.15225147	126.4
6CH3(Z)	-562.20765140	0.0
6CH3(E)	-562.19499357	33.2

Figure S1. M06-2X optimized geometries of **7**(Z)/**7**(E), **8**(Z)/**8**(E), **9**F(Z)/**9**F(E), **10**CH3(Z)/**10**CH3 using basis set aug-cc-pVQZ . (Grey = carbon; white = hydrogen; red = oxygen; yellow = sulfur; blue = nitrogen)

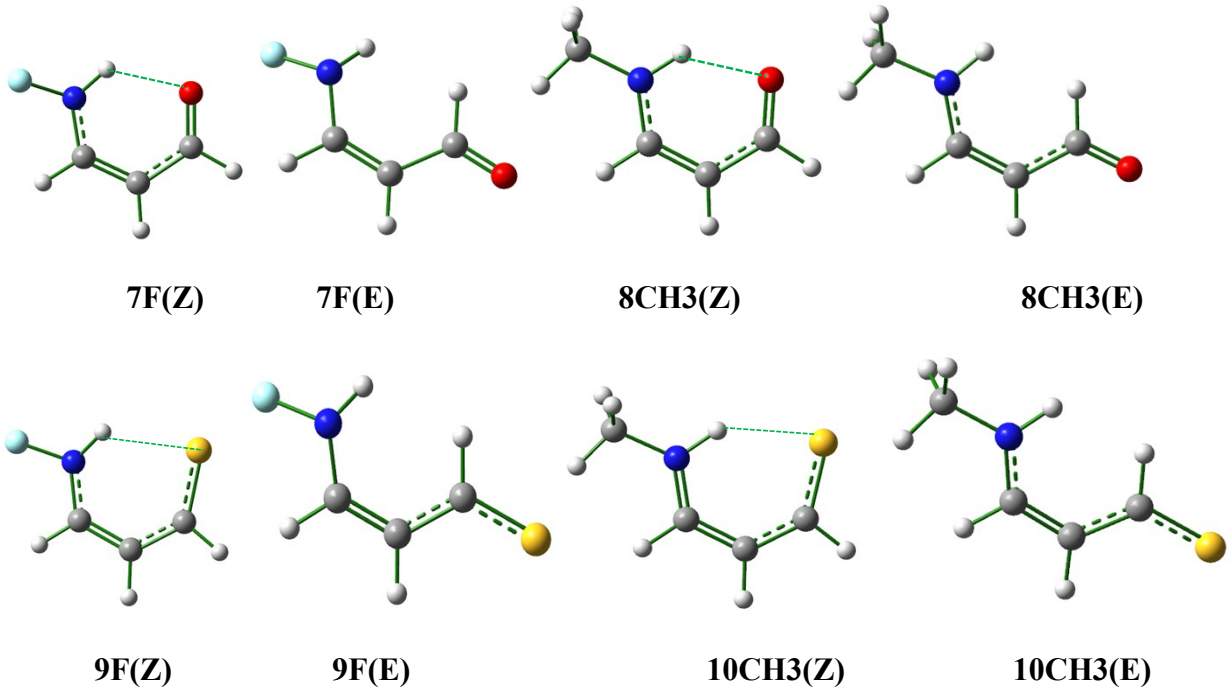


Table S3 The calculated second order perturbation energies (E2) for 3F(Z)-6CH3(Z) using NBO analysis at M06-2X/aug-cc-pVQZ method.

Molecules	n→σ*	E_2(kJ/mol)
3F(Z)	O…Te	47.8
4CH3(Z)	O…Te-C	30.7
6CH3(Z)	S…Te-c	90.6

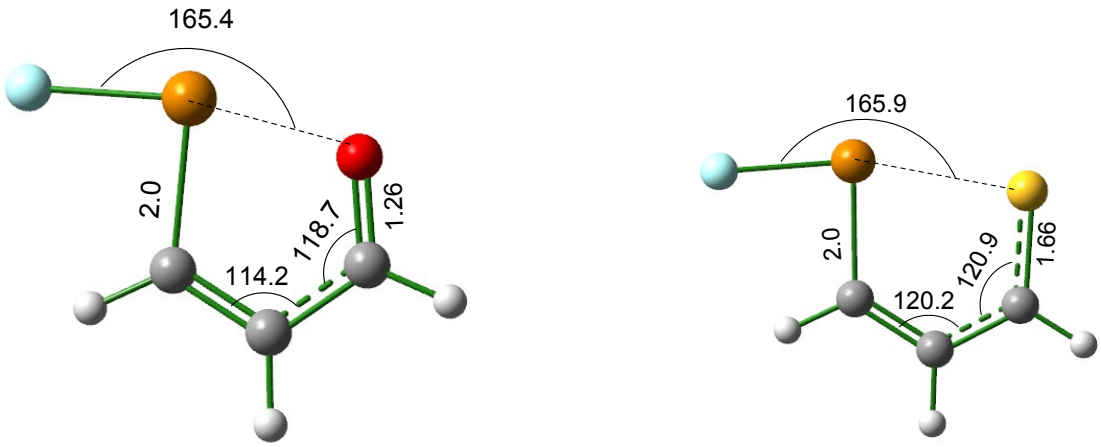
Table S4 Calculated relative energies (KJ/mol) of E/Z isomers of 7(Z)-10(E) at M06-2X/aug-cc-pVQZ method.

Molecules	Energy	ΔE
7F(Z)	-346.46265158	0.0
7F(E)	-346.45149622	29.4
8CH3(Z)	-286.59611142	0.0
8CH3(E)	-286.58301914	34.4
9F(Z)	-669.41944837	0.0
9F(E)	-669.40913691	26.9
10CH3(Z)	-609.55464173	0.0
10CH3(E)	-609.54198133	33.2

Table S5 M06-2X/aug-cc-pVQZ calculated topological parameters (in au) for 3F(Z)-6CH3(Z).

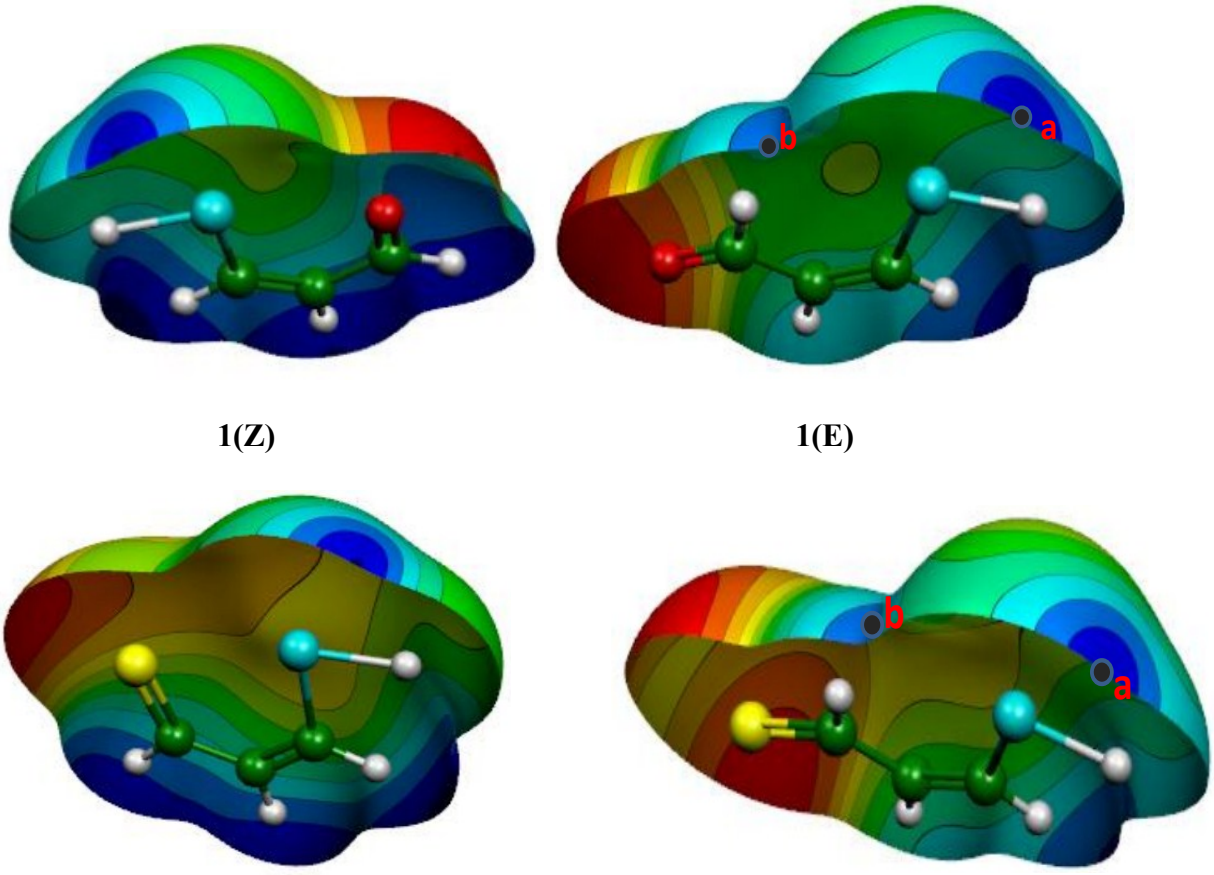
Molecules	P(r)	∇^2 P(r)	G(r)	V(r)	H(r)	V(r)/G(r)
3F(Z)	0.06216	-0.02818	0.03638	-0.07981	-0.04343	2.17
4CH3(Z)	0.02989	0.07512	0.02228	-0.02578	-0.0035	1.16
5F(Z)	0.05826	-0.00451	0.02752	-0.05616	-0.02864	2.04
6CH3(Z)	0.03667	0.04048	0.01765	-0.02518	-0.00753	1.43

Figure S2 Geometrical parameters for 3F(Z) and 5F(Z) compounds. (the bond distances are given in Å)



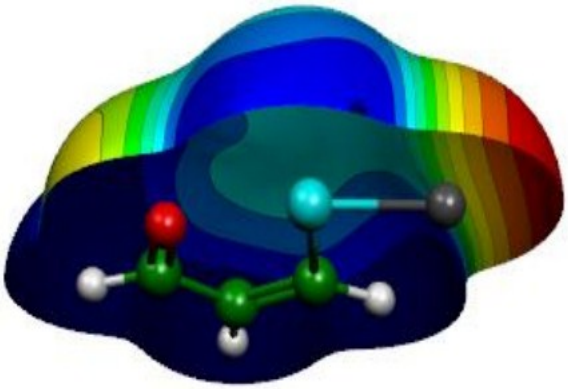
3F(Z) 5F(Z)

Figure S3 The electrostatic potential of compounds 1(Z)-6CH3(E) computed at M06-2X level on the 0.001 au molecular surface (Blue colour point indicate the maximum of eclectrostatic potential (V_{max}) or σ-hole on tellurium atom).

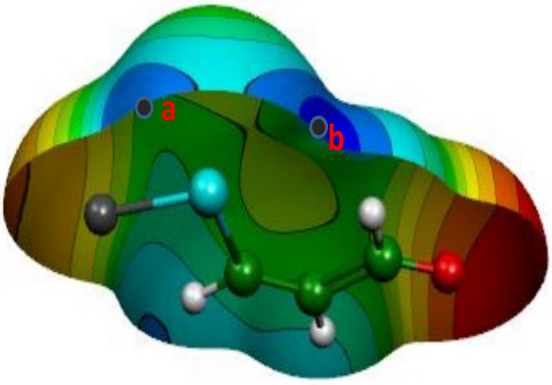


1(Z) **1(E)**

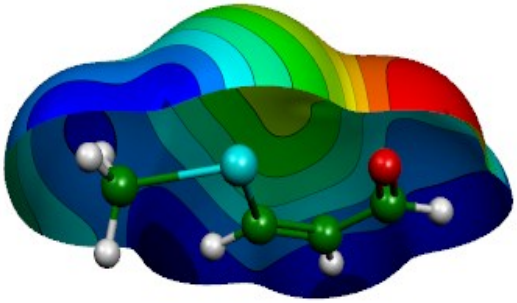
2(Z)



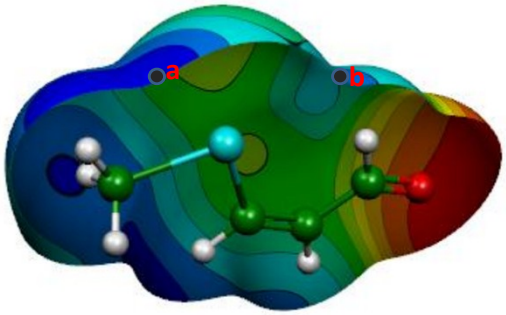
2(E)



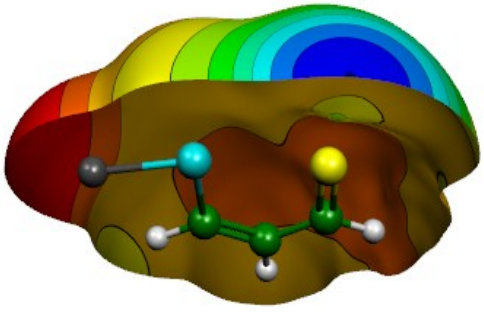
3F(Z)



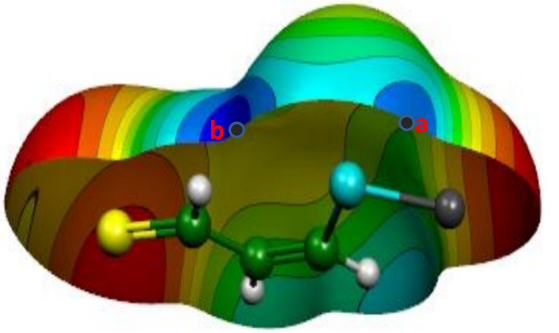
3F(E)



4CH3(Z)

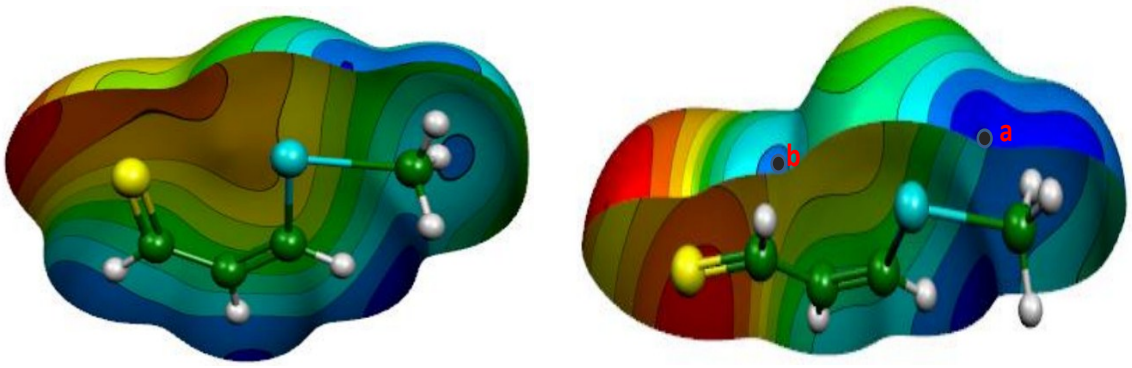


4CH3(E)



***5F(Z)**

5F(E)



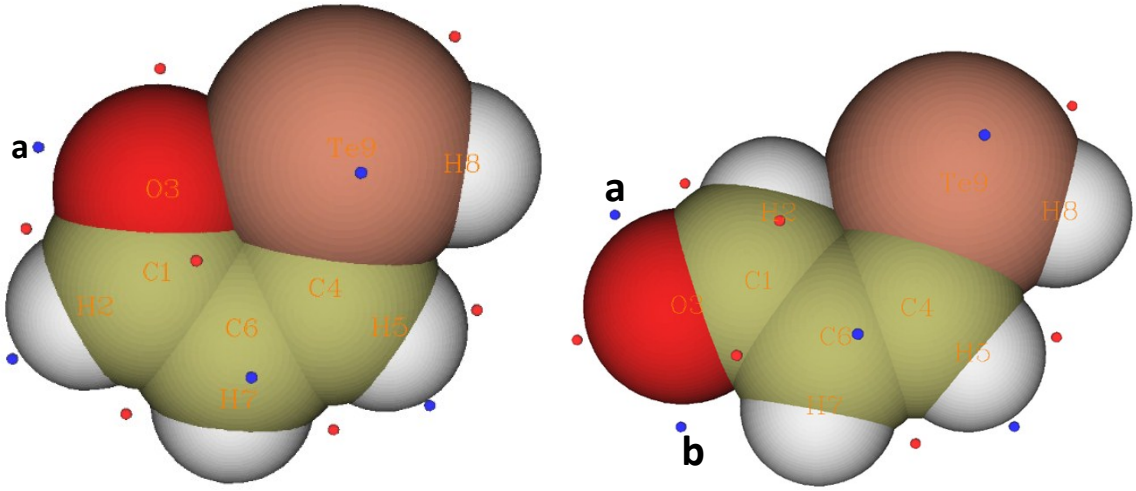
6CH3(Z) **6CH3(E)**

*5F(Z) has shown the V_{max} away from Te and on the top of sulfur atom. This is an exceptional case. We therefore, do not emphasize the MESP result of 5F(Z) for any interpretation.

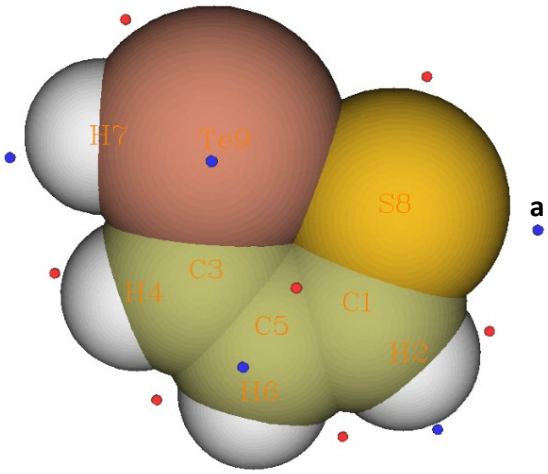
Table S6 The electrostatic potential of σ-hole on tellurium atom. (a & b are two σ-hole on tellurium atom in E-isomer)

Molecules	Bond	V_{max}/σ-hole(Te)	Molecules	V_{max}/ σ-hole(a)(Te)	σ-hole(b)
1(Z)	Te…O	22.28	1(E)	32.38	21.65
2(Z)	Te…S	21.90	2(E)	32.25	23.53
3F(Z)	(F)Te…O	13.93	3F(E)	33.19	39.85
4CH3(Z)	(CH3)Te…O	19.70	4CH3(E)	29.30	17.07
5F(Z)	(F)Te…S	114.14	5F(E)	33.38	40.10
6CH3(Z)	(CH3)Te…S	24.10	6CH3(E)	29.68	19.33

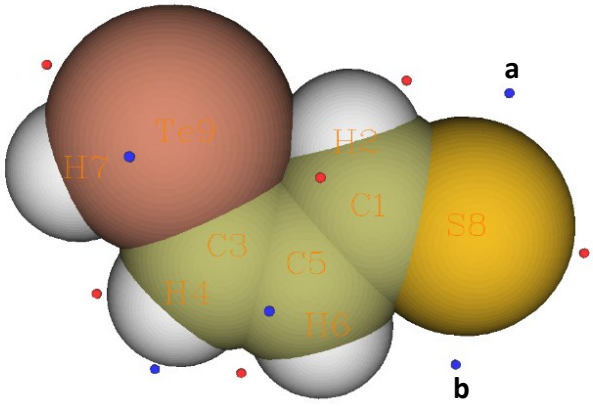
Figure S4 Computed average local ionization energies of 1(Z)-6CH3(E). The blue point (a & b) indicate the local ionization potential on oxygen or sulphur atom.



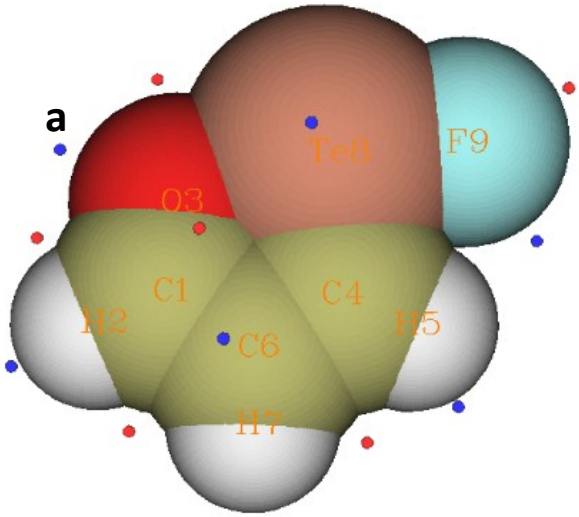
1(Z) **1(E)**


H7
Te9
S8
a
C3
H4
C1
C5
H2
H6

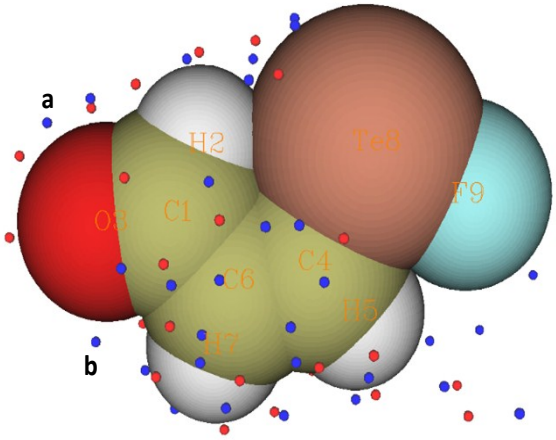
2(Z)


a
Te9
H7
H2
C1
S8
C3
C5
H4
H6
b

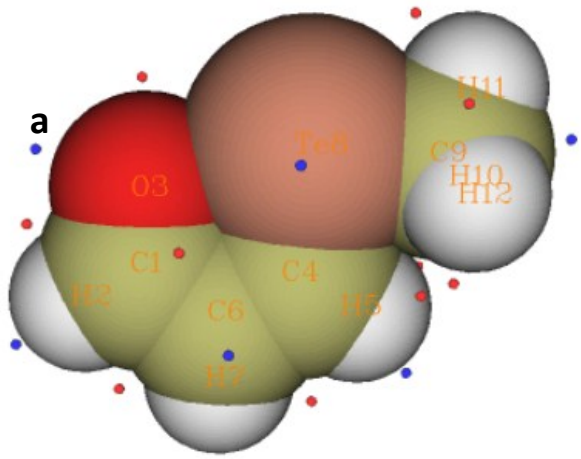
2(E)


a
Te8
F9
O3
C1
C4
H2
H5
C6
H7

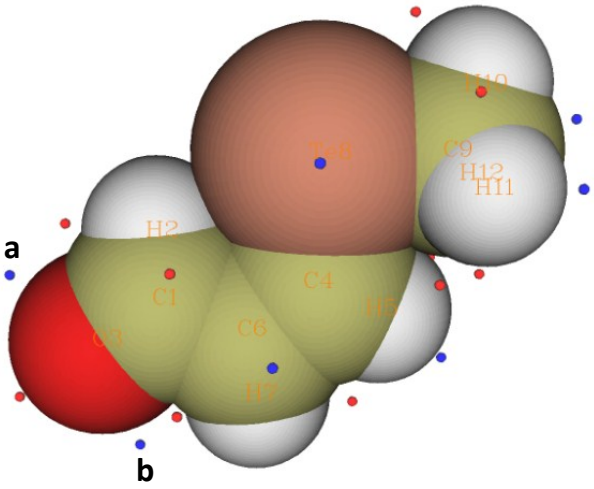
3F(Z)


a
H2
Te8
F9
O3
C1
C4
C6
H5
H7
b

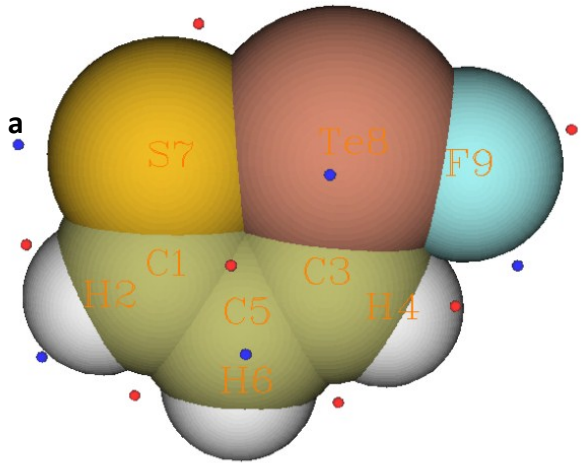
3F(E)



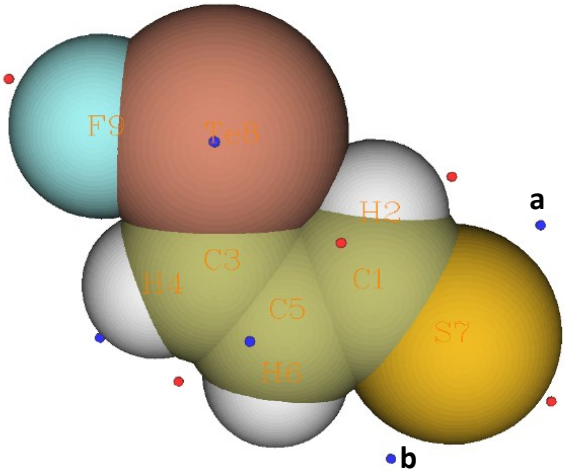
4CH3(Z)



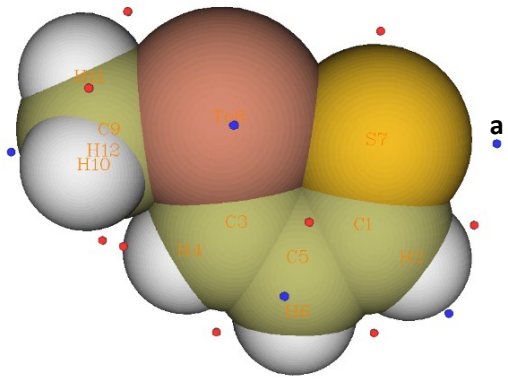
4CH3(E)

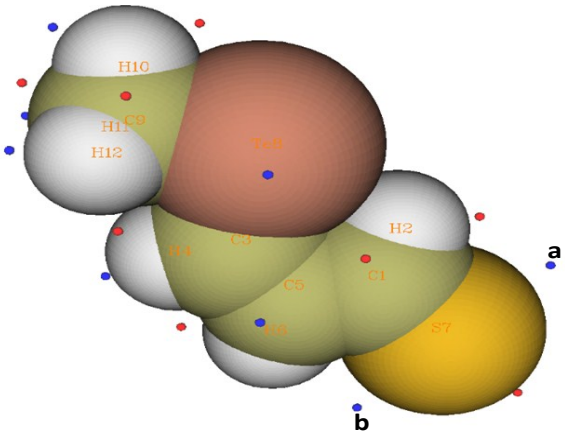


5F(Z)



5F(E)





6CH3(Z) **6CH3(E)**

Table S7 Average local ionization energy data on oxygen/sulphur for 1(Z)-6CH3(E). (I, I(a), I(b) are the average local ionization energy on O/S atom of E/Z isomer of compounds in kcal/mol).

Molecules	Bonds	O/S	I	Molecules	O/S	I(a)	I(b)
1(Z)	Te…O	O	281.75	1(E)	O	276.87	270.32
2(Z)	Te…S	S	207.96	2(E)	S	201.25	200.48
3F(Z)	(F)Te…O	O	305.74	3F(E)	O	280.92	291.24
4CH3(Z)	(CH3)Te…O	O	277.69	4CH3(E)	O	266.48	273.63
5F(Z)	(F)Te…S	S	231.19	5F(E)	S	207.41	206.23
6CH3(Z)	(CH3)Te…S	S	204.21	6CH3(E)	S	197.98	197.04

Table S8. M06-2X optimized Cartesian co-ordinate of compounds 1(Z)-6CH3(Z) using basis set LANL2DZ for tellurium and aug-cc-pVQZ for other atoms in gas phase. (The electronic energies (E) are given in atomic unit).

1(Z)				**1(E)**			
E = -199.93168483				**E = -199.92108177**			
C	-2.32175000	-0.41980500	-0.00008500	C	-0.76267500	-2.23069400	0.00000000
H	-3.39365400	-0.66147800	0.00014700	H	-1.45684100	-1.36451900	0.00000000
O	-1.49641800	-1.31734300	-0.00033900	O	-1.19821300	-3.35016200	0.00000000
C	-0.62819900	1.29410800	-0.00010900	C	1.12062900	-0.64258800	0.00000000
H	-0.31741500	2.32924200	0.00016200	H	2.18840500	-0.47076700	0.00000000
C	-1.93331700	0.97752800	0.00003000	C	0.66460900	-1.89577200	0.00000000
H	-2.70249400	1.73681100	0.00022700	H	1.35009900	-2.73388300	0.00000000
H	2.00364100	1.13785900	-0.00001700	H	1.36866500	2.03590000	0.00000000
Te	0.87847800	-0.09835900	0.00006100	Te	0.00000000	1.11440200	0.00000000
2(Z)				**2(E)**			
E = -522.89026142				**E = -522.87810779**			
C	2.30643100	0.36356400	0.00005800	C	1.96077000	-0.16249800	0.01495400
H	3.38220300	0.50815100	0.00016500	H	1.30621500	-1.03577200	0.04783200
C	0.14336800	1.50587200	0.00012000	C	-0.03305500	1.27759300	-0.00133000
H	-0.39923700	2.44028600	0.00021700	H	-0.43930400	2.27986500	-0.01071900
C	1.49837900	1.53016300	0.00014800	C	1.29867300	1.11694900	-0.00322100
H	2.00201800	2.48846600	0.00025000	H	1.93861300	1.99074300	-0.01647600
H	-2.37316400	0.88073600	0.00006800	H	-2.69126500	0.88530200	0.11746600
S	1.71722900	-1.16639400	0.00004800	S	3.56096300	-0.39015100	-0.00205000
Te	-1.03416400	-0.15486400	-0.00006600	Te	-1.47015400	-0.21673100	-0.00322500
3F(Z)				**3F(E)**			
E = -299.23376410				**E = -299.19591217**			
C	-2.35814800	-0.18742700	0.00005000	C	1.24346000	-2.23527700	0.00000000
H	-3.40197600	-0.49335700	-0.00019500	H	1.76206600	-1.24422900	0.00000000
O	-1.47517000	-1.08741300	0.00012500	O	1.88781500	-3.24490900	0.00000000
C	-0.59543500	1.33373700	0.00002400	C	-0.83115300	-0.96594800	0.00000000

H	-0.11186400	2.29979200	0.00004300
C	-1.95125800	1.15872000	-0.00004600
H	-2.66639800	1.96557300	-0.00008500
Te	0.54518300	-0.31206500	-0.00003400
F	2.11790400	0.81383600	0.00009500

4CH3(Z)

E = -239.24771591

C	2.60429100	-0.02031900	-0.00018200
H	3.70277400	-0.04488200	-0.00053500
O	1.97303200	-1.06507800	-0.00031300
C	0.59769200	1.30035500	0.00027400
H	0.07401700	2.24832600	0.00043600
C	1.94279800	1.26756400	0.00005800
H	2.53847200	2.16923300	0.00006900
Te	-0.58897700	-0.36603200	0.00012500
C	-2.37725100	0.81579900	-0.00049900
H	-2.42718300	1.43438300	-0.89105200
H	-3.22277500	0.13252400	-0.00088200
H	-2.42791700	1.43432700	0.89005100

5F(Z)

E = -622.20023849

C	2.38406500	0.53257600	0.00002900
H	3.45840000	0.65901900	-0.00030200
C	0.17772100	1.46930300	0.00011600
H	-0.50958900	2.30363400	0.00007400
C	1.53764800	1.64007400	-0.00005000
H	1.96362600	2.63409200	-0.00017100
S	1.76870000	-1.01391000	0.00004300
Te	-0.69795700	-0.32650500	-0.00002200
F	-2.39049500	0.63914900	0.00003200

6CH3(Z)

E = -562.20765140

C	2.48008600	0.65204000	-0.00016500
H	3.52221800	0.95432100	-0.00012800
C	0.17009500	1.44302700	-0.00022700
H	-0.51306000	2.28294100	-0.00041500
C	1.50637400	1.68114200	-0.00038700
H	1.85587900	2.70565900	-0.00066600
S	2.12059900	-0.94940400	0.00002400
Te	-0.74266100	-0.36884400	0.00006700
C	-2.67938600	0.59258800	0.00021200
H	-2.80214000	1.20166900	-0.89050400
H	-3.43518700	-0.18874700	0.00032800
H	-2.80193000	1.20172400	0.89092100

7F(Z)

E = -346.46265158

C	-0.91838400	1.08778300	0.01034600
C	0.42051100	0.90097400	-0.05517900
C	-1.81659300	-0.03978100	0.06372800
O	-1.45295700	-1.20193500	-0.01165400
N	1.01038800	-0.30005400	-0.23529400
H	1.12010300	1.72578600	-0.02752700
H	-1.30863500	2.09021800	0.06614800
H	-2.88503400	0.18742400	0.20195300
H	0.52675700	-1.14394500	0.06252800
F	2.33161600	-0.31527500	0.14709200

H	-1.91431700	-0.89926100	0.00000000
C	-0.21842400	-2.15001100	0.00000000
H	-0.77114000	-3.08000600	0.00000000
Te	0.00000000	0.92217100	0.00000000
F	-1.70471400	1.70414100	0.00000000

4CH3(E)

E = -239.23775792

C	2.62420600	-0.22314700	0.00006200
H	1.98239000	-1.12830400	-0.00012600
O	3.82126400	-0.33267200	-0.00018300
C	0.57409600	1.13593800	0.00010500
H	0.11004000	2.11609500	0.00011900
C	1.90668400	1.05452600	0.00009500
H	2.51991100	1.94691300	0.00010900
Te	-0.82094500	-0.40537900	0.00003000
C	-2.47327700	0.93111000	-0.00018500
H	-3.37442200	0.32513500	-0.00028400
H	-2.45467500	1.54536500	0.89308200
H	-2.45446400	1.54534500	-0.89346000

5F(E)

E = -622.15225147

C	2.17118500	-0.08535200	0.00059400
H	1.54085300	-0.98313100	0.00148100
C	0.11408000	1.21881300	-0.00019300
H	-0.40359400	2.17201200	-0.00080800
C	1.45461200	1.16363800	0.00012300
H	2.04266500	2.07222200	-0.00012000
S	3.77342200	-0.27541400	-0.00014000
Te	-1.18664800	-0.37131500	-0.00008300
F	-2.69869100	0.74125500	0.00031600

6CH3(E)

E = -562.19499357

C	2.25122800	-0.09930200	0.00006600
H	1.66447400	-1.01981000	0.00016900
C	0.14892600	1.16912400	-0.00009900
H	-0.33668000	2.13831900	-0.00016400
C	1.49124300	1.12260800	-0.00004000
H	2.05846600	2.04527100	-0.00007000
S	3.86615800	-0.20455700	0.00015500
Te	-1.18632200	-0.41061900	-0.00007400
C	-2.89106600	0.85769600	0.00019200
H	-3.76728400	0.21640300	0.00017900
H	-2.89531100	1.47197400	0.89356100
H	-2.89543200	1.47216900	-0.89304300

7F(E)

E = -346.45149622

C	-0.73426800	0.78966900	-0.01737000
C	0.59948500	0.72519100	0.07553900
C	-1.61495800	-0.37459100	-0.01436500
O	-2.81555200	-0.30774800	-0.06311900
H	1.20737400	1.61955000	0.06202100
H	-1.20637700	1.75743800	-0.09257200
H	-1.12644900	-1.36813200	0.02752300
N	1.35493200	-0.41137200	0.32022300
H	1.01105300	-1.27138000	-0.08957800
F	2.62808200	-0.24861100	-0.21187000

8CH3(Z)

E = -286.59611142

C	-1.01892800	1.06537500	0.00000000
C	0.34279200	0.93847900	0.00000200
C	-1.87188400	-0.08263500	-0.00000200
O	-1.48356800	-1.24706800	0.00000000
N	1.00600600	-0.21522700	0.00000500
H	0.96661100	1.82610800	0.00000000
H	-1.45502300	2.05012600	-0.00000300
H	-2.95574100	0.11789100	-0.00000700
H	0.42127300	-1.04588900	0.00000500
C	2.44407300	-0.32540300	-0.00000300
H	2.79623600	-0.85524300	0.88413800
H	2.79623000	-0.85521400	-0.88416500
H	2.88059300	0.67044800	0.00001200

9F(Z)

E = -669.41944837

C	-0.97109400	0.93907700	0.03593200
C	0.28911100	1.47360300	-0.00192300
C	1.48555200	0.72785600	-0.04239100
S	1.66919000	-0.90899800	0.00254500
N	-1.25688100	-0.35412600	0.15021600
H	0.35012800	2.55026000	-0.03203300
H	-1.84671900	1.57379700	0.01256500
H	2.39014400	1.32446700	-0.12624200
H	-0.58899000	-1.10007700	-0.05759100
F	-2.55942700	-0.68542300	-0.09318200

10CH3(Z)

E = -609.55464173

C	-0.90207600	1.01735700	-0.00000700
C	0.39863400	1.48030400	-0.00000100
C	1.55273200	0.68310500	0.00000700
S	1.68553700	-0.96918600	-0.00000100
N	-1.28384200	-0.24774600	-0.00001200
H	0.52292300	2.55230700	0.00000500
H	-1.71085100	1.74033000	-0.00000400
H	2.48520000	1.24226800	0.00002300
H	-0.53055500	-0.93938300	-0.00000800
C	-2.66225400	-0.67945700	0.00000900
H	-2.87853600	-1.27662700	-0.88415200
H	-2.87856100	-1.27648400	0.88426100
H	-3.31353000	0.19092700	-0.00007100

8CH3(E)

E = -286.58301914

C	0.81915600	0.78475100	0.00508600
C	-0.53241700	0.73416300	-0.03981200
C	1.67721600	-0.37791100	0.01383600
O	2.88599500	-0.34864300	0.03460300
H	-1.08316400	1.66802800	-0.01211900
H	1.29915200	1.75018000	0.03952600
H	1.16878200	-1.36442500	0.00868800
N	-1.33713900	-0.34717400	-0.15123500
H	-0.91522100	-1.25868100	-0.12248000
C	-2.76089700	-0.27743900	0.09364700
H	-3.13080500	0.69046800	-0.23694900
H	-3.27255500	-1.04573600	-0.48008200
H	-3.01252500	-0.40185000	1.14869600

9F(E)

E = -669.40913691

C	-0.17626700	0.83469300	-0.00808300
C	1.16266600	0.73127800	0.06953800
C	-1.07902200	-0.28091400	0.01817100
H	1.79603800	1.60704700	0.04935100
H	-0.60488600	1.82277700	-0.08108100
H	-0.63021400	-1.27197200	0.08281800
N	1.87655800	-0.42945100	0.29979000
H	1.50716400	-1.27291600	-0.12286100
F	3.16265700	-0.30585300	-0.20796500
S	-2.69451200	-0.17727800	-0.03955200

10CH3(E)

E = -609.54198133

C	-1.11197600	0.75095300	-0.02622900
C	0.24715800	0.84500400	0.00142200
C	1.12838800	-0.26697300	0.00255000
S	2.75879400	-0.20871700	0.01413600
N	-1.86937900	-0.35806500	-0.10517100
H	0.68014500	1.83318600	0.02220700
H	-1.69209100	1.66626800	-0.00302200
H	0.66556500	-1.25468700	-0.00031500
H	-1.40915000	-1.25175800	-0.09228000
C	-3.30485200	-0.34996700	0.06839700
H	-3.76196800	-1.10171400	-0.57010300
H	-3.59789000	-0.54206800	1.10179400
H	-3.69196600	0.62259500	-0.22510500