Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Halogen Bond Shortens and Strengthens the Bridge Bond of [1.1.1]Propellane and Open Form of [2.2.2]Propellane

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Supporting Information

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A Detailed Analysis of the Highest Occupied Molecular Orbital (HOMO) of [1.1.1]propellane.

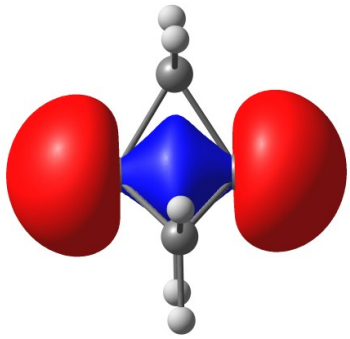

Fig. S1 The highest occupied molecular orbital of [1.1.1]propellane.

The nature of the highest occupied molecular orbital (HOMO) of [1.1.1]propellane remains a mystery even after four decades of active research in this area.[1-4] The presence of two electrons in the outward projecting HOMO resembles diradicaloid character of the central bond. However, extended Huckel calculations of Stohrer and Hoffmann suggested that it is a closed shell orbital with paired electrons, which results in higher stability of the bridge bond structure over the diradicaloid one.[2] Followed by the successful synthesis of [1.1.1]propellane,[3] Wiberg estimated the strength of the bridge bond as much as 65 kcal/mol.[5] However, Newton and Schulman suggested anti-bonding character of this central bond.[1] Deformation density analysis and orbital overlap population also supported this argument.[5, 6] Considering all the experimental and computational evidences, Jackson and Allen proposed the σ-bridged π-bond pattern for the central bond in [1.1.1]propellane, similar to the 3c-2e bonding in electron deficient molecules.[7] Recently, with the aid of valance bond theory and atoms in molecules, Shaik and coworkers proposed that the bridge bond in [1.1.1]propellane is a charge-shift bond.[4] By definition, charge-shift bond is a new kind of chemical bond resulting from the mixing of covalent and ionic structures.[8] Thus, based on our current understanding, there exists a central bond in [1.1.1]propellane with nearly 65 kcal/mol bond strength, and the HOMO being anti-bonding in nature.

A signature for the anti-bonding character of the central bond in [1.1.1]propellane has come from the C_1---C_3 bond stretch analysis, wherein stretching the central bond results in stabilization of the HOMO orbital.[2, 7] We have recomputed the orbital energies of [1.1.1]propellane as a function of the central C_1---C_3 bond (Walsh diagram) using density functional B3LYP-D3/Def2-TZVP level of theory, as shown in Fig. S2.

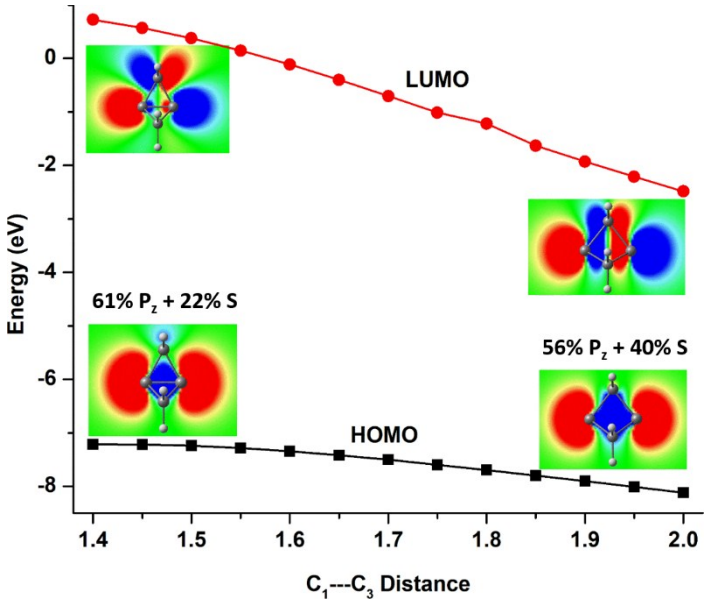

Fig. S2 Walsh diagram for the [1.1.1]propellane molecule. HOMO and LUMO energies are plotted against the C_1---C_3 bond distance. Percentage contribution of s- and p- orbitals to the sp-hybrid HOMO orbital is given. Calculations are done at the B3LYP-D3/Def2-TZVP level of theory.

Figure S2 demonstrates the stabilization of the HOMO upon stretching the C_1---C_3 bond. This observation in the literature is attributed to the anti-bonding character of this orbital. However, we have also observed a change in the hybridization of the bridgehead carbon on going from a compressed geometry ($s^{22}p_z^{61}$) to a stretched one ($s^{40}p_z^{56}$). Thus, the stabilization of the HOMO upon stretching the C_1---C_3 bond could also be due to a change in the hybridization of the bridgehead carbons, wherein an increase in the s-character stabilizes the HOMO. We have also computed the change in Wiberg bond index (WBI) for the C_1---C_3 bond as function of C_1---C_3 distance, Figure S3. On contrary to the anti-bonding arguments, Wiberg bond index decrease as we stretch the C_1---C_3 bond. It could be attributed to the decrease in the bonding character of the HOMO and an increase in its non-bonding character as evident from Figure S3.

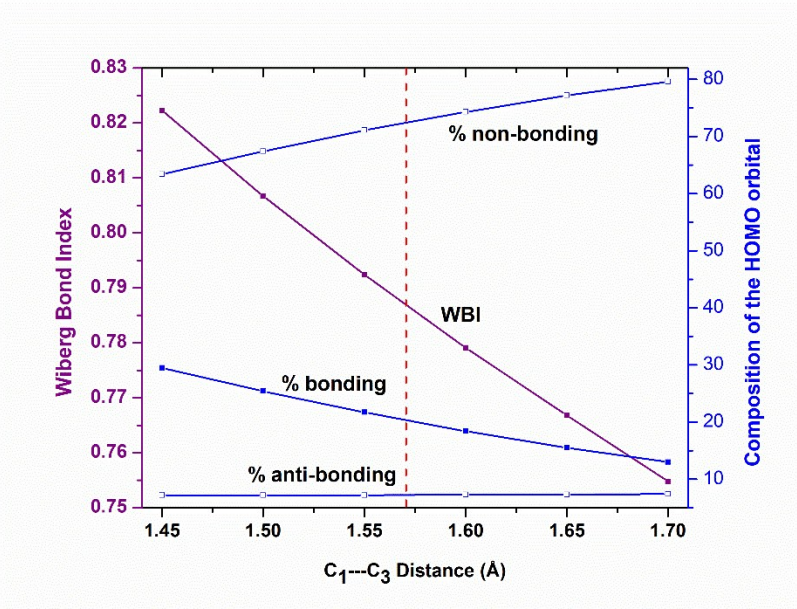

Figure S3. Plot of Wiberg bond index (WBI) and percentage contribution of bonding, non-bonding, and anti-bonding components to the HOMO of [1.1.1]propellane as a function of C_1---C_3 distance. The dashed line represents the equilibrium geometry. Calculations are done at B3LYP-D3/Def2-TZVP level of theory using the NBO-6 program package. Canonical molecular orbital (CMO) analysis implemented in the NBO-6 is used to compute the composition of the HOMO orbital.

However, extending the Walsh diagram by including other orbitals (HOMO-9 to LUMO) is shown in Figure S3. It is interesting to note that HOMO, H-1, and H-2 have no substantial change in energy as compared to H-3, H-4, H-8 and H-9 orbitals along the C_1---C_3 stretching coordinate. It could be inferred that compressing the C_1---C_3 bond below the equilibrium geometry (dashed line) enormously stabilizes the degenerate H-3 and H-4 orbitals (e'), and the H-9 ($1a_1$') orbital with the expense of destabilization from the H-8 orbital ($1a_2$''). The destabilizing effect of HOMO ($2a_1$') and degenerate H-1 and H-2 orbitals (e'') are negligible here. Thus, the equilibrium geometry is a fine balance between the interactions coming from orbitals H-3 to H-9. Thus, removal of an electron from the predominantly non-bonding HOMO orbital (20.6% bonding, 72.2% non-bonding and 7.2% anti-bonding) could reduce the bond order without any major change in the C_1---C_3 bond length.

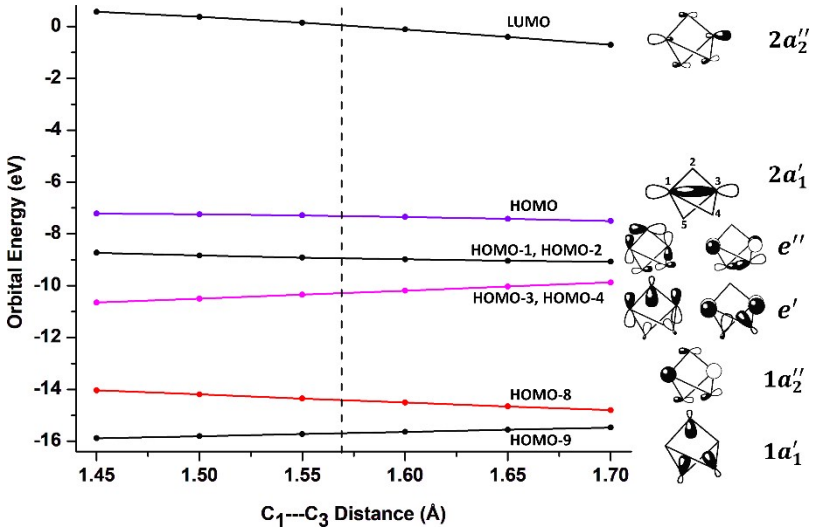

Fig. S4 Walsh diagram for the [1.1.1]propellane molecule. Orbital energies are plotted against the C_1---C_3 bond distance. The dashed line represents the equilibrium geometry.

Our study of the cations resulted in 29.61 mÅ reduction in the C_1---C_3 bond with a decrease in the bond order by 0.19. Here, the HOMO of the cation has 13.6% bonding, 83.2% non-bonding and 3.2% anti-bonding character. The decrease in the bonding component leads to the reduction in bond order. However, it is the stabilization coming from π-framework orbitals $1a_1$' and e' results in shorter C_1---C_3 bond. This stabilization outweighs the destabilization from the $1a_2$'' orbital. Thus, shortening and strengthening of the C_1---C_3 bond in [1.1.1]propellane could be anticipated by extracting a fraction of electrons from its HOMO orbital. We achieve this target by employing electron scavenging halogen bond donors.[9]

References

1. M. D. Newton and J. M. Schulman, *J. Am. Chem. Soc.*, 1972, **94**, 773-778.
2. W. D. Stohrer and R. Hoffmann, *J. Am. Chem. Soc.*, 1972, **94**, 779-786.
3. K. B. Wiberg and F. H. Walker, *J. Am. Chem. Soc.*, 1982, **104**, 5239-5240.
4. W. Wu, J. Gu, J. Song, S. Shaik and P. C. Hiberty, *Angew. Chem., Int. Ed.*, 2009, **48**, 1407-1410.
5. K. B. Wiberg, *J. Am. Chem. Soc.*, 1983, **105**, 1227-1233.
6. P. Chakrabarti, P. Seiler, J. D. Dunitz, A. D. Schluter and G. Szeimies, *J. Am. Chem. Soc.*, 1981, **103**, 7378-7380.
7. J. E. Jackson and L. C. Allen, *J. Am. Chem. Soc.*, 1984, **106**, 591-599.
8. S. Shaik, D. Danovich, W. Wu and P. C. Hiberty, *Nat Chem*, 2009, **1**, 443-449.
9. J. Joy and E. D. Jemmis, *Chem. Commun.*, 2017, **53**, 8168-8171.

Table S1. Selected geometrical and electronic parameters of the neutral and radical cation of [1.1.1] and open form of [2.2.2] propellane. d(C_b-C_b), ν(C_b-C_b), WBI(C_b-C_b) and δ(C_b-C_b) represent the bond length, vibrational frequency, Wiberg bond index, and delocalization index at the bridge bond (C_b-C_b). Calculations are done at the B3LYP-D3/Def2-TZVP level of theory.

	d(C_b-C_b) (Å)	ν(C_b-C_b) (cm^{-1})	WBI (C_b-C_b)	δ (C_b-C_b)
[1.1.1]	1.566	918	0.79	0.74
$[1.1.1]^+$	1.537	961	0.60	0.69
o-[2.2.2]	2.532	805	0.18	0.19
o-$[2.2.2]^+$	2.342	833	0.14	0.16

Table S2. Selected geometrical and electronic parameters of the halogen bonded complexes of [1.1.1]propellane, *o*-[2.2.2]propellane, and *c*-[2.2.2]propellane. $\Delta E^{ZPE\text{-}BSSE}$ represents the zero-point and basis set superposition error corrected binding energy of the halogen bond. ΔG represents the free energy change during the halogen bond formation. d(C_b-C_b), ν(C_b-C_b), WBI(C_b-C_b) and δ(C_b-C_b) represent the bond length, vibrational frequency, Wiberg bond index, and delocalization index at the bridge bond (C_b-C_b). Calculations are done at the B3LYP-D3/Def2-TZVP level of theory.

Acceptor	Donor	$\Delta E^{ZPE\text{-}BSSE}$ kcal/mol	ΔG kcal/mol	d (Å)	ν (cm^{-1})	WBI	δ
[1.1.1]	---	---		1.566	918	0.788	0.737
	ClF	-13.25	+2.15	1.557	940	0.605	0.594
	C_6F_5I	-7.96	+7.16	1.558	928	0.717	0.676
	CF_3I	-7.81	+6.63	1.559	927	0.715	0.674
o-[2.2.2]	---	---		2.532	805	0.178	0.189
	ClF	-22.34	-5.55	2.469	812	0.084	0.103
	C_6F_5I	-11.32	+3.76	2.507	812	0.155	0.158
	CF_3I	-11.30	+2.15	2.506	811	0.154	0.157
c-[2.2.2]	---	---		1.534	1093	0.963	0.914
	ClF	-6.77	+9.73	1.570	860	0.903	0.856
	C_6F_5I	-7.31	+7.41	1.540	901	0.949	0.902
	CF_3I	-7.00	+10.05	1.539	902	0.950	0.901

Table S3. Atomic volume of the carbon atoms of the [1.1.1]propellane molecule in its neutral, cationic, and halogen bonded cases. Quantum theory of atoms in molecules (QTAIM) as implemented in the AIMALL package is used for the calculations by considering 0.001 au isosurface as the volume boundary.

Propellane	Atomic Volume of C_1/C_3 ($Å^3$)	Atomic Volume of $C_2/C_4/C_5$ ($Å^3$)
[1.1.1]	96.62	70.79
$[1.1.1]^+$	81.95	70.76
F-Cl···[1.1.1]···Cl-F	72.19	70.36
C_6F_5-I···[1.1.1]··· I-F_5C_6	86.29	70.88
CF_3-I···[1.1.1]··· I-CF_3	86.25	70.96

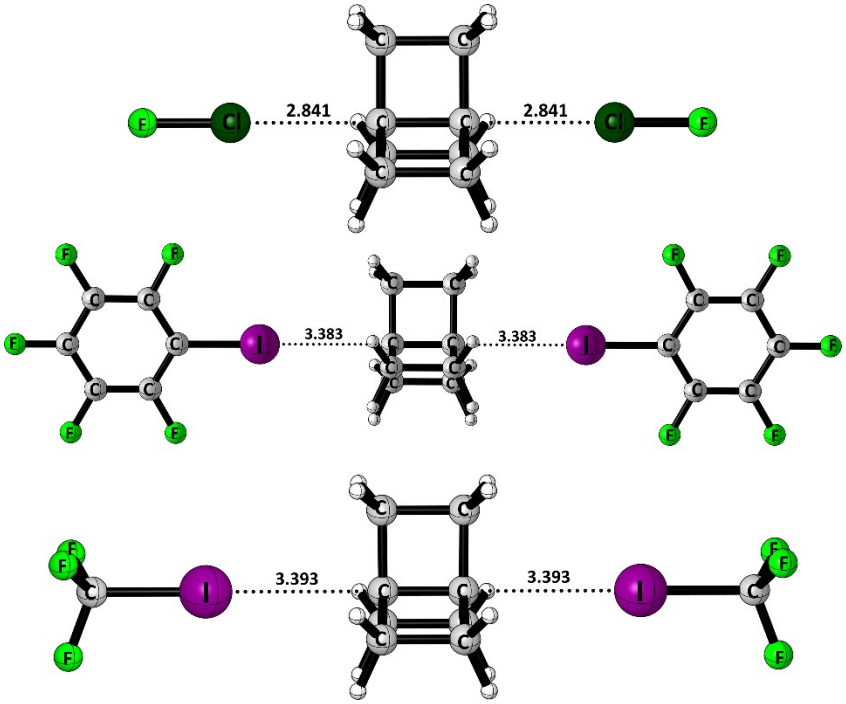

Fig. S5 Optimized structures of the halogen bonded complexes of the closed form of [2.2.2]propellane. Calculations are done at the B3LYP-D3/Def2TZVP level of theory.

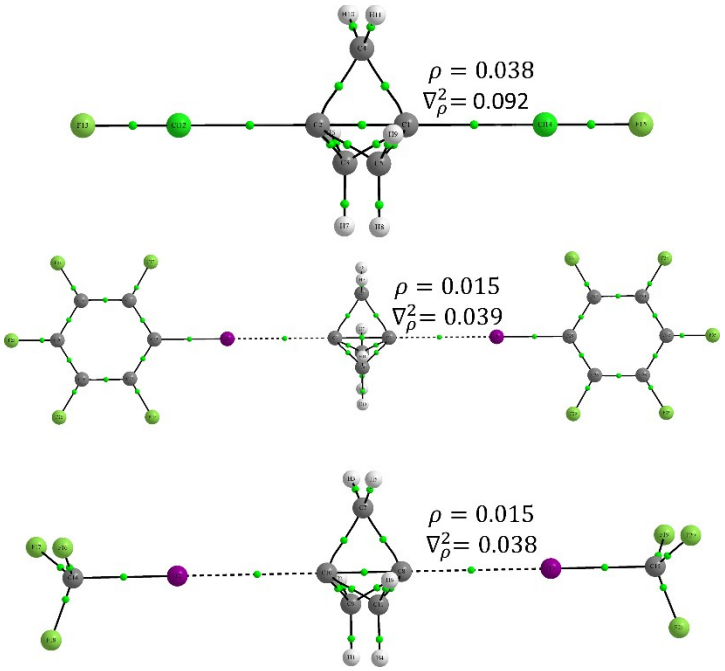

Fig. S6 Topological map of the halogen bonded complexes of [1.1.1]propellane. Calculations are done using AIMALL package with wavefunction files generated from the B3LYP-D3/Def2-TZVP calculation.

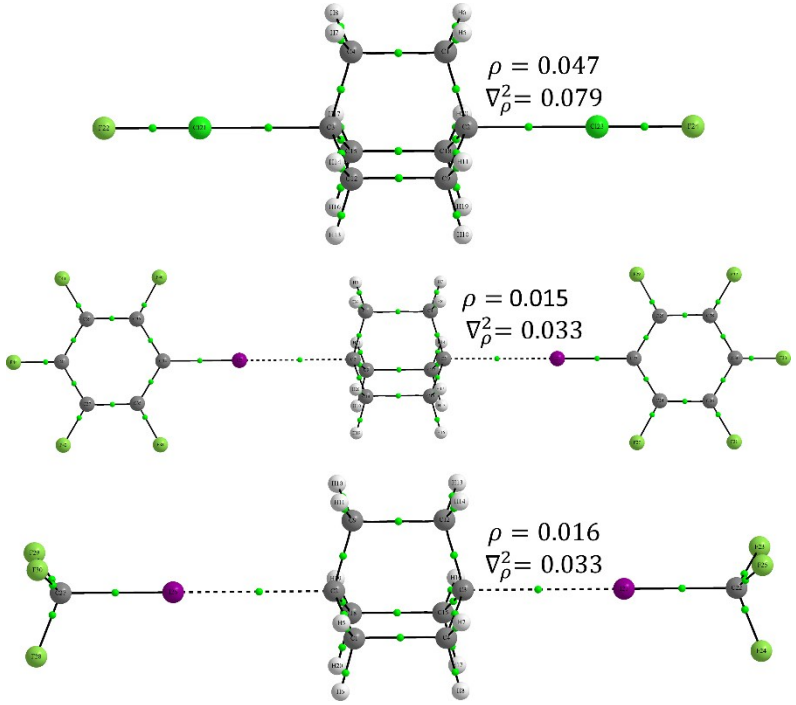

Fig. S7 Topological map of the halogen bonded complexes of *o*-[2.2.2]propellane. Calculations are done using AIMALL package with wavefunction files generated from the B3LYP-D3/Def2-TZVP calculation.

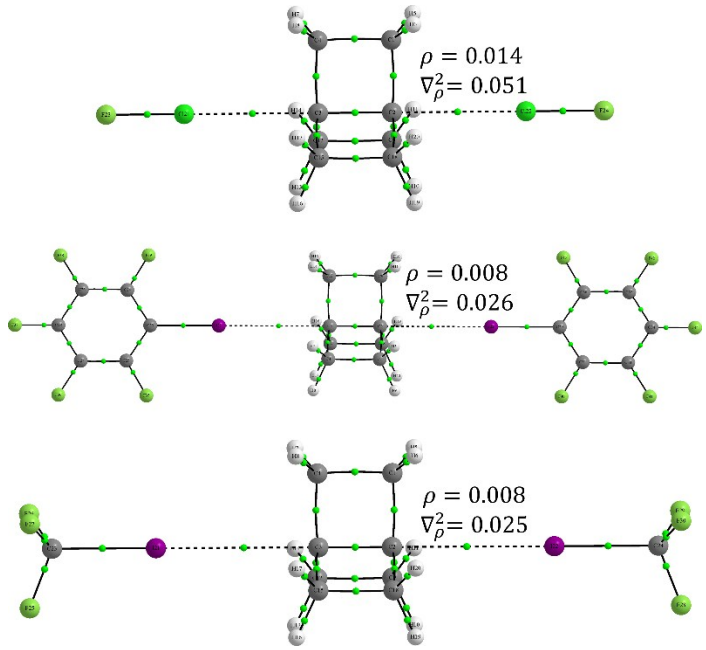

Fig. S8 Topological map of the halogen bonded complexes of *c*-[2.2.2]propellane. Calculations are done using AIMALL package with wavefunction files generated from the B3LYP-D3/Def2-TZVP calculation.

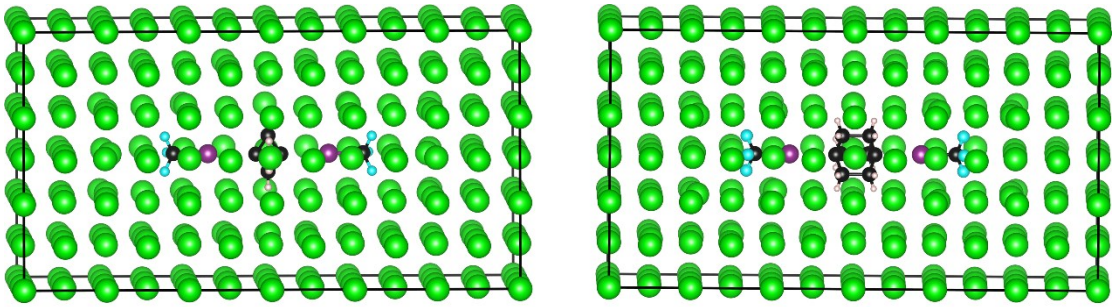

Fig. S9 Halogen bond (CF_3I) adducts of [1.1.1] and *o*-[2.2.2] propellane inside the cavity of an argon matrix consisting of more than 300 argon atoms. Calculations are done at dispersion corrected periodic density functional PBE using the VASP package.

Cartesian Coordinates of the complexes studied.

Geometry optimizations are carried out at B3LYP-D3/Def2-TZVP level of theory using Gaussian09-D01.

(1) ClF

Sum of electronic and zero-point Energies = -560.031035
Sum of electronic and thermal Energies = -560.028591
Sum of electronic and thermal Enthalpies = -560.027647
Sum of electronic and thermal Free Energies = -560.052369

Cl	0.000000000	0.000000000	0.568263000
F	0.000000000	0.000000000	-1.073386000

(2) C_6F_5I

Sum of electronic and zero-point Energies= -1025.862171
Sum of electronic and thermal Energies= -1025.851851
Sum of electronic and thermal Enthalpies= -1025.850907
Sum of electronic and thermal Free Energies= -1025.899238

I	0.000000000	0.000000000	2.301807000
C	0.000000000	0.000000000	0.209825000
C	0.000000000	1.194203000	-0.503223000
C	0.000000000	-1.194203000	-0.503223000
C	0.000000000	1.201320000	-1.891416000
F	0.000000000	2.369147000	0.129231000
C	0.000000000	-1.201320000	-1.891416000
F	0.000000000	-2.369147000	0.129231000
C	0.000000000	0.000000000	-2.587045000
F	0.000000000	2.354770000	-2.559315000
F	0.000000000	-2.354770000	-2.559315000
F	0.000000000	0.000000000	-3.917255000

(3) CF_3I

Sum of electronic and zero-point Energies= -635.569322
Sum of electronic and thermal Energies= -635.564529
Sum of electronic and thermal Enthalpies= -635.563584
Sum of electronic and thermal Free Energies= -635.598567

I	0.000000000	0.000000000	0.979791000
C	0.000000000	0.000000000	-1.191731000
F	0.000000000	1.249035000	-1.658464000
F	1.081696000	-0.624517000	-1.658464000
F	-1.081696000	-0.624517000	-1.658464000

(4) [1.1.1]propellane

Sum of electronic and zero-point Energies= -193.990622
Sum of electronic and thermal Energies= -193.986654
Sum of electronic and thermal Enthalpies= -193.985710
Sum of electronic and thermal Free Energies= -194.015224

C	0.000000000	0.000000000	0.783239000
C	0.000000000	0.000000000	-0.783239000
C	0.000000000	1.297550000	0.000000000
C	-1.123712000	-0.648775000	0.000000000
C	1.123712000	-0.648775000	0.000000000
H	-0.913366000	1.879744000	0.000000000
H	0.913366000	1.879744000	0.000000000
H	2.084589000	-0.148874000	0.000000000
H	1.171223000	-1.730871000	0.000000000
H	-2.084589000	-0.148874000	0.000000000
H	-1.171223000	-1.730871000	0.000000000

(5) *o*-[2.2.2]propellane

Sum of electronic and zero-point Energies= -311.925045
Sum of electronic and thermal Energies= -311.918641
Sum of electronic and thermal Enthalpies= -311.917697
Sum of electronic and thermal Free Energies= -311.953370

C	0.000000000	1.393008000	0.916466000
C	0.000000000	0.000000000	1.265837000
C	0.000000000	0.000000000	-1.265837000
C	0.000000000	1.393008000	-0.916466000
H	-0.897917000	1.947384000	1.175426000
H	0.897917000	1.947384000	1.175426000
H	-0.897917000	1.947384000	-1.175426000
H	0.897917000	1.947384000	-1.175426000
C	-1.206380000	-0.696504000	0.916466000
H	-1.237526000	-1.751311000	1.175426000
H	-2.135443000	-0.196073000	1.175426000
C	-1.206380000	-0.696504000	-0.916466000
H	-1.237526000	-1.751311000	-1.175426000
H	-2.135443000	-0.196073000	-1.175426000
C	1.206380000	-0.696504000	-0.916466000
H	1.237526000	-1.751311000	-1.175426000
H	2.135443000	-0.196073000	-1.175426000
C	1.206380000	-0.696504000	0.916466000
H	1.237526000	-1.751311000	1.175426000
H	2.135443000	-0.196073000	1.175426000

(6) *c*-[2.2.2]propellane

Sum of electronic and zero-point Energies= -311.909619
Sum of electronic and thermal Energies= -311.902719
Sum of electronic and thermal Enthalpies= -311.901775
Sum of electronic and thermal Free Energies= -311.940624

C	-1.108063000	-1.083281000	-0.786254000
C	0.000054000	-0.000101000	-0.766969000
C	0.000144000	-0.000116000	0.766968000
C	-1.107945000	-1.083324000	0.786352000
H	-0.811760000	-2.028869000	-1.243344000
H	-2.046655000	-0.765179000	-1.243125000
H	-0.811508000	-2.028926000	1.243332000
H	-2.046484000	-0.765333000	1.243415000
C	1.492254000	-0.417791000	-0.786400000
H	2.162564000	0.312160000	-1.243261000
H	1.686619000	-1.389432000	-1.243568000
C	1.492343000	-0.417751000	0.786240000
H	2.162666000	0.312283000	1.242952000
H	1.686844000	-1.389344000	1.243451000
C	-0.384289000	1.501073000	0.786344000
H	0.360142000	2.155197000	1.243320000
H	-1.351491000	1.716753000	1.243377000
C	-0.384373000	1.501078000	-0.786283000
H	0.359960000	2.155247000	-1.243354000
H	-1.351647000	1.716720000	-1.243185000

(7) FCl···[1.1.1]···ClF

Sum of electronic and zero-point Energies= -1314.076222
Sum of electronic and thermal Energies= -1314.064608
Sum of electronic and thermal Enthalpies= -1314.063664
Sum of electronic and thermal Free Energies= -1314.116529

C	0.000000000	0.000000000	0.778540000
C	0.000000000	0.000000000	-0.778540000
C	-0.557453000	1.176821000	0.000000000
C	-0.740431000	-1.071179000	0.000000000
C	1.297883000	-0.105642000	0.000000000
H	-1.632053000	1.306751000	0.000000000
H	0.023398000	2.090172000	0.000000000
H	1.947707000	0.760024000	0.000000000
H	1.798443000	-1.065350000	0.000000000
H	-1.821841000	-1.024823000	0.000000000
H	-0.315653000	-2.066775000	0.000000000
Cl	0.000000000	0.000000000	-3.225214000
F	0.000000000	0.000000000	-4.913368000
Cl	0.000000000	0.000000000	3.225214000
F	0.000000000	0.000000000	4.913368000

(8) $CF_3I\cdots[1.1.1]\cdots IF_3C$

Sum of electronic and zero-point Energies= -1465.142217
Sum of electronic and thermal Energies= -1465.124582
Sum of electronic and thermal Enthalpies= -1465.123638
Sum of electronic and thermal Free Energies= -1465.201795

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H	2.085766000	-0.148454000	0.000000000
H	0.914318000	1.880553000	0.000000000
H	-1.171448000	-1.732099000	0.000000000
H	-0.914318000	1.880553000	0.000000000
H	-2.085766000	-0.148454000	0.000000000
C	0.000000000	1.300489000	0.000000000
C	0.000000000	0.000000000	0.779372000
C	1.126256000	-0.650244000	0.000000000
C	0.000000000	0.000000000	-0.779372000
C	-1.126256000	-0.650244000	0.000000000
I	0.000000000	0.000000000	-3.897968000
I	0.000000000	0.000000000	3.897968000
C	0.000000000	0.000000000	-6.076792000
C	0.000000000	0.000000000	6.076792000
F	-1.082220000	0.624820000	-6.552261000
F	1.082220000	0.624820000	-6.552261000
F	0.000000000	-1.249640000	-6.552261000
F	1.082220000	0.624820000	6.552261000
F	-1.082220000	0.624820000	6.552261000
F	0.000000000	-1.249640000	6.552261000

(9) $C_6F_5I\cdots[1.1.1]\cdots IF_5C_6$

Sum of electronic and zero-point Energies= -2245.728025
Sum of electronic and thermal Energies= -2245.698469
Sum of electronic and thermal Enthalpies= -2245.697524
Sum of electronic and thermal Free Energies= -2245.802284

C	0.000000000	0.778970000	-0.006132000
C	0.000000000	-0.778970000	-0.006132000
C	0.000000000	0.000000000	1.294731000
C	1.126621000	0.000000000	-0.656055000
C	-1.126621000	0.000000000	-0.656055000
H	0.914476000	0.000000000	1.874417000
H	-0.914476000	0.000000000	1.874417000
H	-2.085984000	0.000000000	-0.154102000
H	-1.171742000	0.000000000	-1.737942000
H	2.085984000	0.000000000	-0.154102000
H	1.171742000	0.000000000	-1.737942000
I	0.000000000	3.891171000	-0.002281000
C	0.000000000	5.996328000	0.000555000

C	-1.191917000	6.712302000	0.001487000
C	1.191917000	6.712302000	0.001487000
C	-1.200816000	8.100514000	0.003314000
F	-2.369235000	6.080945000	0.000660000
C	1.200816000	8.100514000	0.003314000
F	2.369235000	6.080945000	0.000660000
C	0.000000000	8.796591000	0.004234000
F	-2.355086000	8.769215000	0.004194000
F	2.355086000	8.769215000	0.004194000
F	0.000000000	10.127808000	0.005972000
I	0.000000000	-3.891171000	-0.002281000
C	0.000000000	-5.996328000	0.000555000
C	1.191917000	-6.712302000	0.001487000
C	-1.191917000	-6.712302000	0.001487000
C	1.200816000	-8.100514000	0.003314000
F	2.369235000	-6.080945000	0.000660000
C	-1.200816000	-8.100514000	0.003314000
F	-2.369235000	-6.080945000	0.000660000
C	0.000000000	-8.796591000	0.004234000
F	2.355086000	-8.769215000	0.004194000
F	-2.355086000	-8.769215000	0.004194000
F	0.000000000	-10.127808000	0.005972000

(10) FCl··· *o*-[2.2.2]···ClF

Sum of electronic and zero-point Energies= -1432.025489
Sum of electronic and thermal Energies= -1432.010860
Sum of electronic and thermal Enthalpies= -1432.009916
Sum of electronic and thermal Free Energies= -1432.066946

C	0.000000000	1.408967000	0.860912000
C	0.000000000	0.000000000	1.234558000
C	0.000000000	0.000000000	-1.234558000
C	0.000000000	1.408967000	-0.860912000
H	-0.892321000	1.948850000	1.165091000
H	0.892321000	1.948850000	1.165091000
H	-0.892321000	1.948850000	-1.165091000
H	0.892321000	1.948850000	-1.165091000
C	-1.220201000	-0.704484000	0.860912000
H	-1.241593000	-1.747198000	1.165091000
H	-2.133914000	-0.201652000	1.165091000
C	-1.220201000	-0.704484000	-0.860912000
H	-1.241593000	-1.747198000	-1.165091000
H	-2.133914000	-0.201652000	-1.165091000
C	1.220201000	-0.704484000	-0.860912000
H	1.241593000	-1.747198000	-1.165091000
H	2.133914000	-0.201652000	-1.165091000
C	1.220201000	-0.704484000	0.860912000
H	1.241593000	-1.747198000	1.165091000

H	2.133914000	-0.201652000	1.165091000
Cl	0.000000000	0.000000000	-3.622668000
F	0.000000000	0.000000000	-5.371687000
Cl	0.000000000	0.000000000	3.622668000
F	0.000000000	0.000000000	5.371687000

(11) $CF_3I\cdots$*o*-[2.2.2]$\cdots IF_3C$

Sum of electronic and zero-point Energies= -1583.082342
Sum of electronic and thermal Energies= -1583.061532
Sum of electronic and thermal Enthalpies= -1583.060588
Sum of electronic and thermal Free Energies= -1583.147075

C	0.896159000	0.739759000	1.186253000
C	1.253053000	0.000244000	-0.000218000
C	-1.253050000	0.000296000	-0.000284000
C	-0.896187000	0.739792000	1.186209000
H	1.169899000	0.270301000	2.126945000
H	1.169915000	1.791055000	1.179035000
H	-1.169994000	0.270343000	2.126885000
H	-1.169903000	1.791099000	1.178980000
C	0.896224000	-1.396991000	0.046851000
H	1.169934000	-1.976864000	-0.830100000
H	1.169865000	-1.916502000	0.960876000
C	-0.896281000	-1.396955000	0.046800000
H	-1.169964000	-1.976812000	-0.830170000
H	-1.169995000	-1.916458000	0.960807000
C	-0.896115000	0.658189000	-1.233929000
H	-1.169865000	0.126417000	-2.140856000
H	-1.169829000	1.707593000	-1.297607000
C	0.896209000	0.658149000	-1.233885000
H	1.169982000	0.126364000	-2.140796000
H	1.169972000	1.707541000	-1.297551000
I	-4.388539000	0.000049000	0.000244000
C	-6.580016000	-0.000277000	-0.000009000
F	-7.057597000	-0.618539000	-1.086584000
F	-7.058037000	1.249686000	0.007798000
F	-7.057927000	-0.632205000	1.078525000
I	4.388538000	-0.000054000	-0.000005000
C	6.580015000	-0.000196000	0.000180000
F	7.057938000	1.249653000	0.021192000
F	7.057867000	-0.607002000	-1.092717000
F	7.057753000	-0.643359000	1.072127000

(12) $C_6F_5I\cdots$*o*-[2.2.2]$\cdots IF_5C_6$

Sum of electronic and zero-point Energies= -2363.668050
Sum of electronic and thermal Energies= -2363.636097
Sum of electronic and thermal Enthalpies= -2363.635153
Sum of electronic and thermal Free Energies= -2363.745855

C	-0.724404000	1.189796000	-0.894954000
C	-0.011278000	-0.011497000	-1.247677000
C	-0.008878000	-0.012922000	1.259013000
C	-0.722740000	1.188673000	0.907671000
H	-0.234356000	2.121033000	-1.164239000
H	-1.776636000	1.205855000	-1.164345000
H	-0.232585000	2.119798000	1.177225000
H	-1.774489000	1.204499000	1.179025000
C	1.388547000	0.006136000	-0.886469000
H	1.948765000	-0.881927000	-1.165965000
H	1.925888000	0.908559000	-1.164841000
C	1.390195000	0.005177000	0.893845000
H	1.951224000	-0.883044000	1.171291000
H	1.928267000	0.907190000	1.172216000
C	-0.691879000	-1.231314000	0.908799000
H	-0.178386000	-2.150518000	1.175611000
H	-1.743322000	-1.274003000	1.178189000
C	-0.693605000	-1.230355000	-0.898864000
H	-0.180313000	-2.149072000	-1.167652000
H	-1.745547000	-1.272575000	-1.166301000
I	-0.003536000	-0.007202000	4.396893000
I	-0.009228000	-0.005259000	-4.400116000
C	0.003554000	0.001933000	6.514077000
C	0.003194000	-1.173198000	7.230542000
C	0.007912000	1.183215000	7.220290000
C	0.007139000	-1.176734000	8.604451000
F	-0.001743000	-2.345748000	6.609070000
C	0.012360000	1.198456000	8.594313000
F	0.008406000	2.350529000	6.588657000
C	0.011929000	0.013666000	9.287831000
F	0.006425000	-2.319741000	9.274357000
F	0.016628000	2.347304000	9.254574000
F	0.015769000	0.019213000	10.610086000
C	0.000959000	0.002490000	-6.516668000
C	0.011196000	-1.178966000	-7.234332000
C	-0.002957000	1.189086000	-7.225638000
C	0.017519000	-1.183552000	-8.614882000
F	0.015454000	-2.354802000	-6.609748000
C	0.003095000	1.203739000	-8.606179000
F	-0.012985000	2.360322000	-6.592504000
C	0.013457000	0.012533000	-9.302567000
F	0.027347000	-2.330927000	-9.285917000
F	-0.000851000	2.356068000	-9.268926000
F	0.019394000	0.017330000	-10.629171000

(13) FCl··· *c*-[2.2.2]···ClF

Sum of electronic and zero-point Energies= -1431.984837
Sum of electronic and thermal Energies= -1431.969737
Sum of electronic and thermal Enthalpies= -1431.968793
Sum of electronic and thermal Free Energies= -1432.029848

C	0.000000000	1.553442000	0.780821000
C	0.000000000	0.000000000	0.784775000
C	0.000000000	0.000000000	-0.784775000
C	0.000000000	1.553442000	-0.780821000
H	0.882369000	1.998272000	1.241080000
H	-0.882369000	1.998272000	1.241080000
H	0.882369000	1.998272000	-1.241080000
H	-0.882369000	1.998272000	-1.241080000
C	1.345320000	-0.776721000	0.780821000
H	1.289370000	-1.763290000	1.241080000
H	2.171739000	-0.234982000	1.241080000
C	1.345320000	-0.776721000	-0.780821000
H	1.289370000	-1.763290000	-1.241080000
H	2.171739000	-0.234982000	-1.241080000
C	-1.345320000	-0.776721000	-0.780821000
H	-1.289370000	-1.763290000	-1.241080000
H	-2.171739000	-0.234982000	-1.241080000
C	-1.345320000	-0.776721000	0.780821000
H	-1.289370000	-1.763290000	1.241080000
H	-2.171739000	-0.234982000	1.241080000
Cl	0.000000000	0.000000000	-3.626120000
Cl	0.000000000	0.000000000	3.626120000
F	0.000000000	0.000000000	-5.281239000
F	0.000000000	0.000000000	5.281239000

(14) CF_3I···*c*-[2.2.2]···IF_3C

Sum of electronic and zero-point Energies= -1583.059847
Sum of electronic and thermal Energies= -1583.039295
Sum of electronic and thermal Enthalpies= -1583.038351
Sum of electronic and thermal Free Energies= -1583.121732

C	0.000000000	1.552238000	0.784701000
C	0.000000000	0.000000000	0.769970000
C	0.000000000	0.000000000	-0.769970000
C	0.000000000	1.552238000	-0.784701000
H	0.882839000	2.000177000	1.242451000
H	-0.882839000	2.000177000	1.242451000
H	0.882839000	2.000177000	-1.242451000
H	-0.882839000	2.000177000	-1.242451000
C	1.344277000	-0.776119000	0.784701000
H	1.290785000	-1.764649000	1.242451000
H	2.173624000	-0.235527000	1.242451000

C	1.344277000	-0.776119000	-0.784701000
H	1.290785000	-1.764649000	-1.242451000
H	2.173624000	-0.235527000	-1.242451000
C	-1.344277000	-0.776119000	-0.784701000
H	-1.290785000	-1.764649000	-1.242451000
H	-2.173624000	-0.235527000	-1.242451000
C	-1.344277000	-0.776119000	0.784701000
H	-1.290785000	-1.764649000	1.242451000
H	-2.173624000	-0.235527000	1.242451000
I	0.000000000	0.000000000	-4.162928000
I	0.000000000	0.000000000	4.162928000
C	0.000000000	0.000000000	-6.335300000
C	0.000000000	0.000000000	6.335300000
F	0.000000000	-1.249201000	-6.804880000
F	1.081840000	0.624601000	-6.804880000
F	-1.081840000	0.624601000	-6.804880000
F	0.000000000	-1.249201000	6.804880000
F	1.081840000	0.624601000	6.804880000
F	-1.081840000	0.624601000	6.804880000

(15) $C_6F_5I\cdots$*c*-[2.2.2]$\cdots IF_5C_6$

Sum of electronic and zero-point Energies= -2363.646013
Sum of electronic and thermal Energies= -2363.613428
Sum of electronic and thermal Enthalpies= -2363.612484
Sum of electronic and thermal Free Energies= -2363.727293

C	0.784669000	1.423693000	-0.637998000
C	0.769581000	0.004277000	-0.009641000
C	-0.769590000	0.004238000	-0.009576000
C	-0.784799000	1.423791000	-0.637621000
H	1.242333000	1.475666000	-1.626655000
H	1.243050000	2.190512000	-0.012400000
H	-1.243013000	1.476181000	-1.626001000
H	-1.242699000	2.190465000	-0.011491000
C	0.784725000	-1.249819000	-0.924458000
H	1.242673000	-2.131851000	-0.475221000
H	1.242760000	-1.091257000	-1.901528000
C	-0.784743000	-1.249658000	-0.924674000
H	-1.243091000	-2.131728000	-0.475925000
H	-1.242387000	-1.090627000	-1.901852000
C	-0.784680000	-0.161416000	1.533861000
H	-1.242221000	-1.087223000	1.884762000
H	-1.242722000	0.668518000	2.073325000
C	0.784809000	-0.161046000	1.533833000
H	1.242895000	-1.086466000	1.885035000
H	1.242384000	0.669337000	2.073007000
I	-4.153081000	0.001077000	-0.006024000
I	4.153082000	0.001324000	-0.005696000

C	-6.246919000	-0.000778000	0.001239000
C	-6.960112000	-1.194854000	-0.009021000
C	-6.962133000	1.192024000	0.016645000
C	-8.348290000	-1.203711000	-0.004143000
C	-8.350331000	1.198423000	0.021697000
C	-9.045178000	-0.003258000	0.011269000
C	6.246920000	-0.000735000	0.001333000
C	6.959908000	-1.194880000	0.016640000
C	6.962340000	1.191999000	-0.008970000
C	8.348084000	-1.203870000	0.021555000
C	8.350540000	1.198264000	-0.004249000
C	9.045180000	-0.003485000	0.011066000
F	-6.331111000	2.368029000	0.027035000
F	-9.019341000	2.351553000	0.036507000
F	-10.375720000	-0.004445000	0.016018000
F	-9.015356000	-2.358019000	-0.014149000
F	-6.327102000	-2.369749000	-0.023853000
F	6.331519000	2.368065000	-0.023708000
F	9.019749000	2.351329000	-0.014312000
F	9.014952000	-2.358243000	0.036292000
F	6.326696000	-2.369714000	0.027087000
F	10.375723000	-0.004801000	0.015685000

(16) [2.2.2]propellane-MECP1

C	0.793971000	1.281023000	-0.775045000
C	0.000454000	0.000568000	-1.013884000
C	-0.000429000	-0.000523000	1.013894000
C	0.695124000	1.336228000	0.776437000
H	0.353868000	2.148100000	-1.274758000
H	1.823447000	1.182060000	-1.127468000
H	0.083918000	2.170463000	1.129294000
H	1.665133000	1.400530000	1.277010000
C	-1.505665000	0.046954000	-0.776496000
H	-2.035876000	-0.767610000	-1.276732000
H	-1.934325000	0.987990000	-1.129314000
C	-1.505741000	-0.066118000	0.775208000
H	-1.922615000	-1.012517000	1.127516000
H	-2.046657000	0.741708000	1.274981000
C	0.808993000	-1.270919000	0.775608000
H	0.378470000	-2.143535000	1.274482000
H	1.836657000	-1.160246000	1.130194000
C	0.713232000	-1.327143000	-0.775765000
H	0.113846000	-2.169300000	-1.130291000
H	1.684500000	-1.378055000	-1.274657000

(17) [2.2.2]propellane-MECP2

C	-1.433057000	-0.130241000	0.808747000
C	-0.000145000	0.000141000	1.218561000

C	-0.000122000	0.000142000	-1.218561000
C	-1.433042000	-0.130229000	-0.808773000
H	-2.037459000	0.702996000	1.171177000
H	-1.877640000	-1.058330000	1.171287000
H	-2.037427000	0.703024000	-1.171200000
H	-1.877633000	-1.058305000	-1.171335000
C	0.603790000	1.305988000	0.809071000
H	1.627495000	1.412756000	1.171240000
H	0.022375000	2.155213000	1.171290000
C	0.603816000	1.305984000	-0.809058000
H	1.627535000	1.412733000	-1.171194000
H	0.022427000	2.155216000	-1.171302000
C	0.829377000	-1.175894000	-0.809034000
H	1.855265000	-1.096626000	-1.171180000
H	0.409946000	-2.116041000	-1.171347000
C	0.829369000	-1.175890000	0.809048000
H	1.855252000	-1.096610000	1.171204000
H	0.409944000	-2.116039000	1.171361000

(18) $CF_3I\cdots[2.2.2]\cdots IF_3C$ – MECP1

C	0.056342000	0.772034000	1.511648000
C	-0.000042000	1.007734000	0.000025000
C	0.000042000	-1.007734000	0.000025000
C	-0.056342000	-0.772034000	1.511648000
H	-0.754831000	1.276604000	2.038934000
H	0.999219000	1.130346000	1.927796000
H	-0.999219000	-1.130346000	1.927796000
H	0.754831000	-1.276604000	2.038934000
C	-1.337351000	0.771881000	-0.706782000
H	-1.388420000	1.276958000	-1.672611000
H	-2.169423000	1.129985000	-0.098576000
C	-1.280978000	-0.771931000	-0.804689000
H	-1.170451000	-1.130327000	-1.829350000
H	-2.143216000	-1.276459000	-0.365896000
C	1.337351000	-0.771881000	-0.706782000
H	1.388420000	-1.276958000	-1.672611000
H	2.169423000	-1.129985000	-0.098576000
C	1.280978000	0.771931000	-0.804689000
H	1.170451000	1.130327000	-1.829350000
H	2.143216000	1.276459000	-0.365896000
I	-0.000033000	4.003985000	-0.000016000
I	0.000033000	-4.003985000	-0.000016000
C	0.000033000	6.219377000	0.000008000
C	-0.000033000	-6.219377000	0.000008000
F	1.088845000	6.692147000	0.614172000
F	-1.076324000	6.692104000	0.635759000
F	-0.012449000	6.692110000	-1.250011000
F	1.076324000	-6.692104000	0.635759000

F	-1.088845000	-6.692147000	0.614172000
F	0.012449000	-6.692110000	-1.250011000

(19) $CF_3I\cdots[2.2.2]\cdots IF_3C$ – MECP2

C	0.000000000	0.804092000	1.446358000
C	0.000000000	1.208242000	0.002668000
C	0.000000000	-1.208242000	0.002668000
C	0.000000000	-0.804092000	1.446358000
H	-0.883674000	1.171866000	1.967473000
H	0.883674000	1.171866000	1.967473000
H	-0.883674000	-1.171866000	1.967473000
H	0.883674000	-1.171866000	1.967473000
C	-1.248609000	0.804355000	-0.721927000
H	-1.251420000	1.170347000	-1.748351000
H	-2.143863000	1.172953000	-0.221851000
C	-1.248609000	-0.804355000	-0.721927000
H	-1.251420000	-1.170347000	-1.748351000
H	-2.143863000	-1.172953000	-0.221851000
C	1.248609000	-0.804355000	-0.721927000
H	1.251420000	-1.170347000	-1.748351000
H	2.143863000	-1.172953000	-0.221851000
C	1.248609000	0.804355000	-0.721927000
H	1.251420000	1.170347000	-1.748351000
H	2.143863000	1.172953000	-0.221851000
I	0.000000000	-4.072915000	0.000461000
I	0.000000000	4.072915000	0.000461000
C	0.000000000	-6.295224000	-0.001238000
C	0.000000000	6.295224000	-0.001238000
F	0.000000000	-6.768675000	-1.252209000
F	-1.083164000	-6.769839000	0.623739000
F	1.083164000	-6.769839000	0.623739000
F	0.000000000	6.768675000	-1.252209000
F	-1.083164000	6.769839000	0.623739000
F	1.083164000	6.769839000	0.623739000