Conformational stability and structural analysis of methanethiol clusters: a revisit

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Introduction

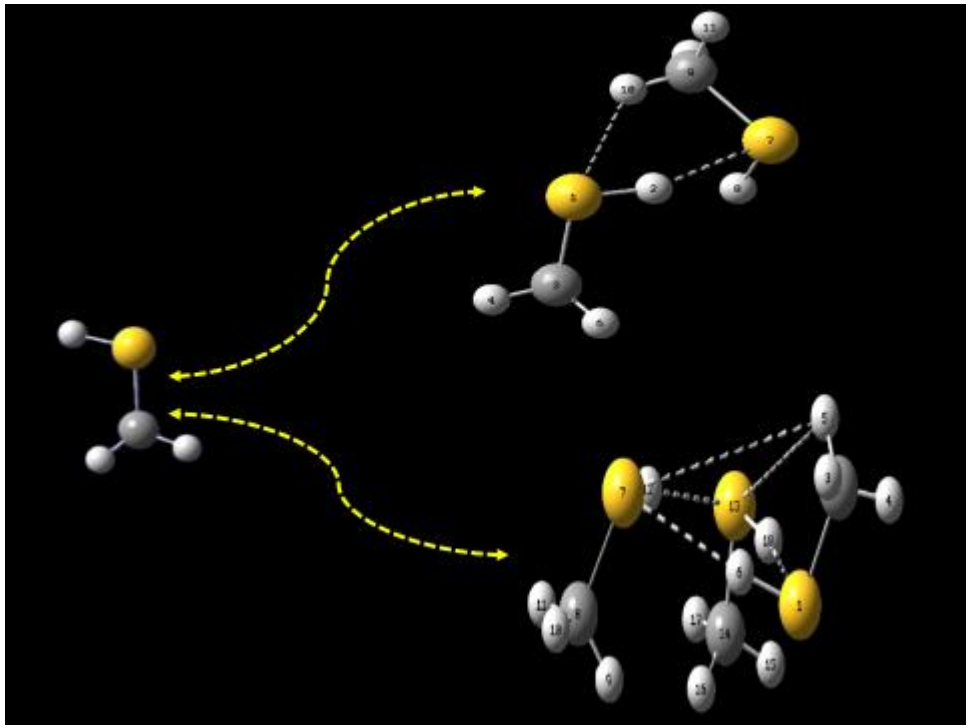
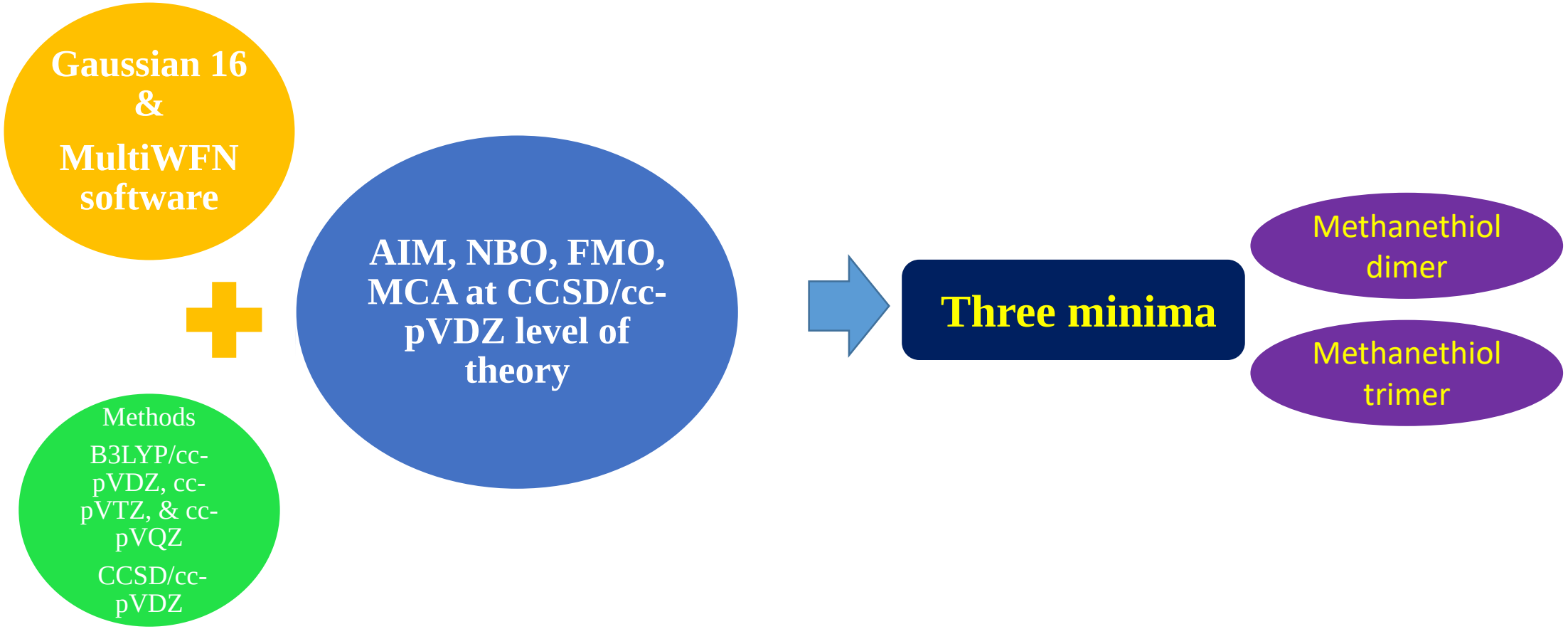


Fig. Non-covalent interactions in methanethiol cluster[3]

- Methanethiol is toxic, colorless gas with a smell like rotten cabbage and found in human blood, brain, and tissues of some animals.
- It's non-covalent interactions in biological systems is of paramount significance given its natural occurrence
- Earlier literatures are erroneous with respect to conformational and structural analysis of methanethiol molecular cluster[1-2].

Computational methods



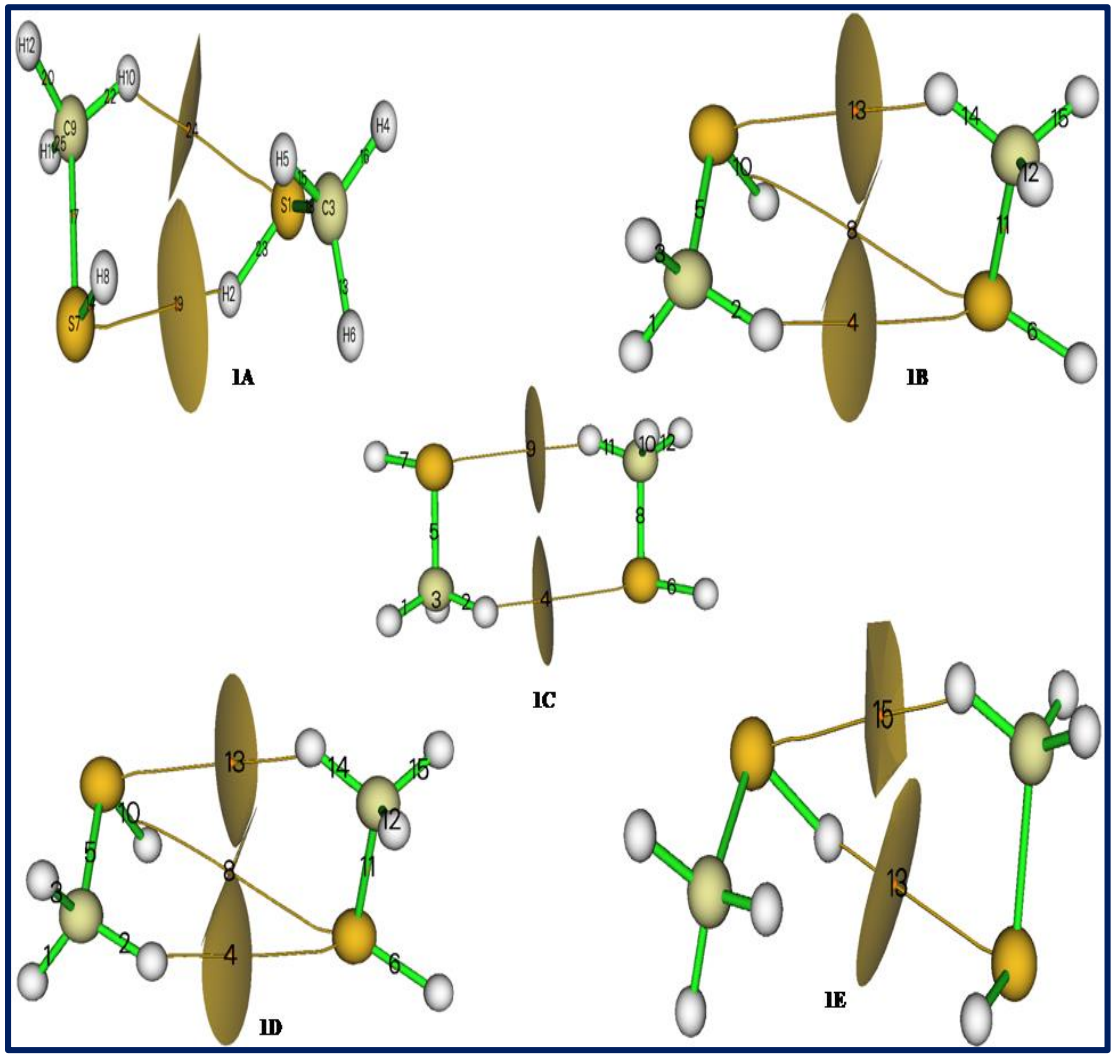
The basis set superposition error (BSSE) was done using the Helgonker method[3]

$$E_{corr} = a + bX^{-3}$$

[where a and b are the constant parameters to be determined and X is a cardinal number, *i.e.*, four for quadruple-zeta sets and five for quintuple-zeta sets.]

The correlation energy was extrapolated at the cc-pVNZ (where N = T, Q).

Result & Discussion



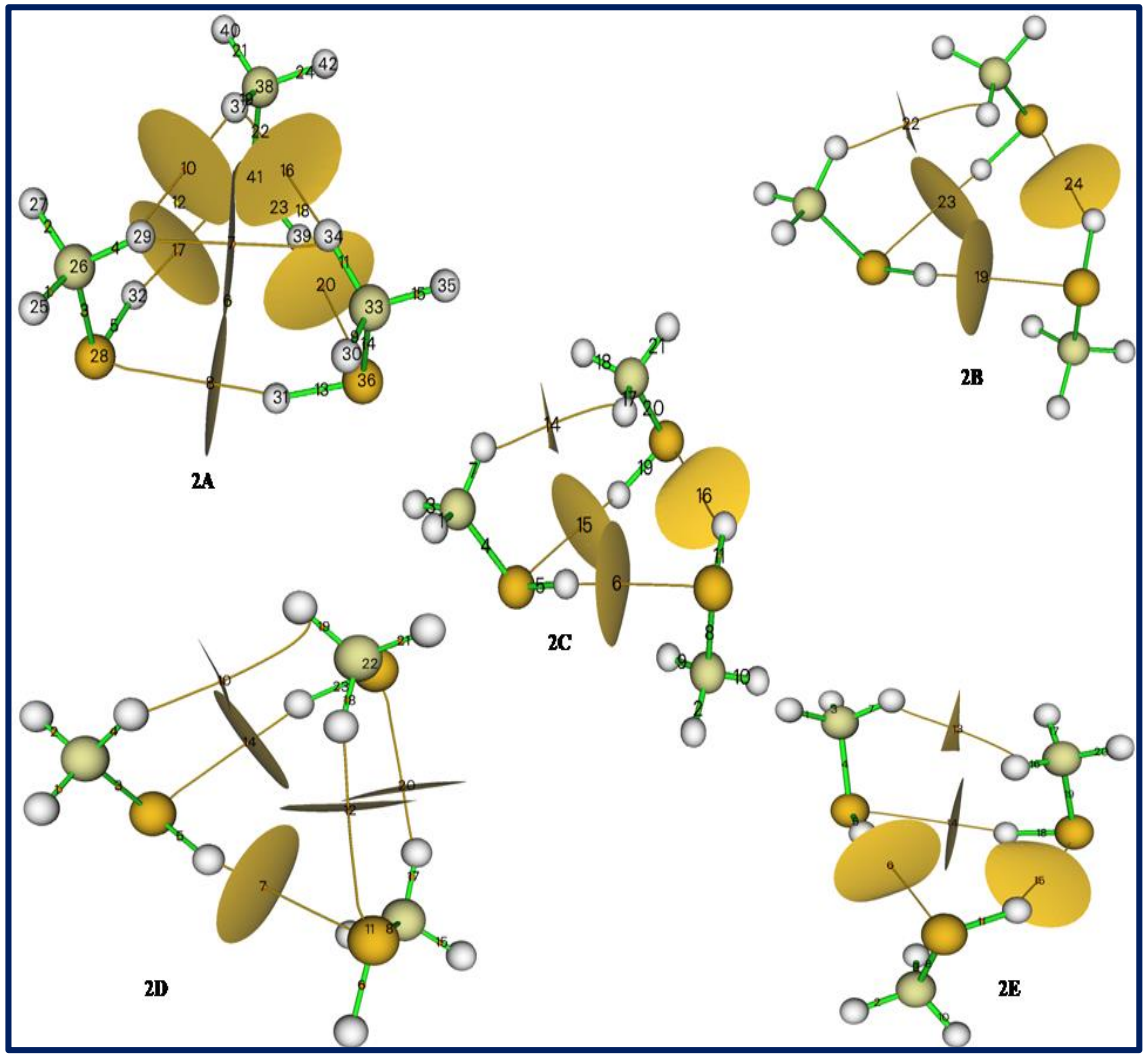


Fig. 3 Topological basin surface with bond critical points (3, -1) of methanethiol dimer & trimer at B3LYP/cc-pVDZ level of theory[3]

Table: 1 Relative change in interaction energy of different conformers of dimer and trimer of the methanethiol molecule[3]

Conformers /methods	Methanethiol Dimer			Methanethiol Trimer		
	1A, 1E	1B, 1D	1C	2B, 2C, 2E	2A	2D
B3LYP/cc-pVDZ	0.00	0.54	1.51	0.00	2.00	2.14
B3LYP/cc-pVTZ	2.67	2.65	3.43	6.22	8.41	7.48
B3LYP/cc-pVQZ	3.24	3.26	3.96	7.38	9.59	8.59
B3LYP/CBS	3.66	3.71	3.96	8.23	10.45	9.40
CCSD/cc-pVDZ	0.78	0.05	0.10	4.80	5.74	3.46

Note: All values in the above table are in kcal/mol and referenced with respect to the most stable dimer and trimer at B3LYP/cc-pVDZ

Table: 2 Absolute value of the S-H vibrational frequency at B3LYP/cc-pVDZ level of theory

This work		Past work from Ref [2]	
S-H stretch	v (cm^{-1})	@MP2/aug-cc-pVDZ (cm^{-1}) (Harmonic)	Experiment (cm^{-1})
1A & 1E (7,8)	2600	2749	2601
(1,2)	2652	2746	
2A (1,3)	2574	2694	2567
(7,9)	2584	2674	
(13,15)	2584	2659	

Note: The values correspond to the most stable structure (erroneously assumed by Lung Fu et al in their work.)

Table: 3 Summary of the computed energy parameter of methanethiol dimer & trimer at CCSD/cc-pVDZ level of theory[3]

	Dimer			Trimer		
Conformer → Energy parameter ↓	1A & 1E	1B & 1D	1C	2A	2B, 2C, & 2E	2D
E_{HOMO} (IP) (kcal mol^{-1})	-220.7	-221.0	-221.8	-222.7	-222.6	-222.5
E_{LUMO} (EA) (kcal mol^{-1})	86.6	90.9	91.0	78.9	89.5	89.5
HOMO-LUMO gap (E_g)	307.3	311.9	312.8	301.6	312.1	312.0
Dipole moment (D)	1.82	1.47	0.00	3.43	1.40	1.80
Hardness (η)	-67.1	-65.1	-65.4	-71.9	-66.6	-66.5
Chemical potential (μ)	67.1	65.1	65.4	71.9	66.6	66.5
Electronegativity (χ)	-67.1	-65.1	-65.4	-71.9	-66.6	-66.5
Electrophilicity index (ω)	-33.6	-32.6	-32.7	-36.0	-33.3	-33.3

Summary

- Three minima in place of five for both dimer and trimer of methanethiol.
- Conformer 1A or 1E and 2E or 2C or 2B are most stable conformer for methanethiol dimer and trimer respectively
- Interaction energy, dipole moment, and geometrical parameter have the same values for the CCSD and B3LYP methods with the cc-pVDZ basis set.
- Our calculated results have good agreement with experimental results

Reference

1. E. M. Cabaleiro-Lago and J. Rodr´ıguez-Otero, Methanethiol dimer and trimer. An ab initio and DFT study of the interaction, J. Phys. Chem. A, 2002, 106(32), 7440–7447.
2. L. Fu, H.-L. Han and Y.-P. Lee, Infrared absorption of methanethiol clusters (CH3SH) n, n = 2–5, recorded with a time-of-flight mass spectrometer using IR depletion and VUV ionization, J. Chem. Phys., 2012, 137(23), 234307.
3. Manish Kumar Tripathi and Venkatnarayan Ramanathan, conformational stability and structural analysis of methanethiol clusters: A revisit, RSC Adv., 2021, 11, 29207.

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