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

Electronic Supplementary Information

Prototypical Cyclohexane Dimers: Spectroscopic Evidence for σ stacking at Low Temperatures

N. Ramanathan,* Shubhra Sarkar and K. Sundararajan

Materials Chemistry and Metal Fuel Cycle Group
Homi Bhabha National Institute
Indira Gandhi Centre for Atomic Research
Kalpakkam 603 102, India

Corresponding Author: nram@igcar.gov.in

Table S1. Relative free energy of cyclohexane dimers and Maxwell-Boltzmann population at 12 K and 32 K calculated using aug-cc- pVDZ basis set with various levels of theory.

Relative Free energy (kcal/mol)			Maxwell-Boltzmann Population (%)					
MP2	B3LYP-D3	B2-PLYP-D3	At 12 K			At 32 K		
			MP2	B3LYP-D3	B2-PLYP-D3	MP2	B3LYP-D3	B2-PLYP-D3
0	0	0.00	99.9	99.9	97.4	94.4	99.9	79.6
0.18	0.49	0.09	0.05	--[b]	2.6	5.6	--[b]	20.4
1.07	1.67	0.72	--[b]	--[b]	--[b]	--[b]	--[b]	--[b]

[b]negligible population

Table S2. Cartesian coordinates of cyclohexane monomer and dimers optimized at MP2 level of theory with aug-cc-pVDZ basis set.

Cyclohexane monomer

Atomic number	X	Y	Z
1	0.434957000	-1.442682000	1.342395000
6	0.421970000	-1.399698000	0.237009000
6	-1.001198000	-1.065287000	-0.236976000
6	1.423151000	-0.334421000	-0.237034000
1	0.722672000	-2.397260000	-0.126904000
6	-1.423162000	0.334433000	0.236969000
1	-1.714735000	-1.824466000	0.127031000
1	-1.032002000	-1.098095000	-1.342356000
6	1.001203000	1.065265000	0.237028000
1	2.437444000	-0.572770000	0.126811000
1	1.466801000	-0.344675000	-1.342425000
6	-0.421943000	1.399710000	-0.236997000
1	-2.437401000	0.572759000	-0.127051000
1	-1.466983000	0.344745000	1.342348000
1	1.031929000	1.097939000	1.342418000
1	1.714757000	1.824495000	-0.126832000
1	-0.722684000	2.397245000	0.126957000
1	-0.434886000	1.442752000	-1.342380000

Cyclohexane Eclipsed (face to face) Dimer-A

Atomic number	X	Y	Z
6	-1.941786000	-1.451856000	0.184077000
1	-2.048227000	-1.514895000	-1.993733000
6	-2.406904000	1.452757000	-0.183286000
1	-2.309630000	0.969828000	-2.307922000
1	-0.836808000	0.584148000	-1.400325000
6	-2.408296000	-0.565794000	1.350323000
1	-2.311082000	-2.483372000	0.315718000
1	-0.837822000	-1.506034000	0.188595000
6	-1.936209000	0.885345000	1.165532000
1	-2.036624000	2.484249000	-0.314839000
1	-3.512272000	1.505429000	-0.188032000
1	-3.513719000	-0.583573000	1.398863000
1	-2.039113000	-0.969272000	2.309120000
1	-2.302293000	1.515288000	1.994332000
1	-0.832131000	0.915736000	1.206525000
1	0.836152000	-0.589819000	1.397341000

6	1.940153000	-0.568629000	1.348261000
6	2.410402000	-1.452435000	0.181861000
6	2.409346000	0.883789000	1.165850000
1	2.308579000	-0.972163000	2.306994000
6	1.939543000	-0.884426000	-1.166626000
1	2.042805000	-2.485107000	0.311618000
1	3.515904000	-1.502016000	0.187857000
6	1.939037000	1.451703000	-0.182895000
1	2.040849000	1.512076000	1.995220000
1	3.514805000	0.914924000	1.206163000
6	2.409041000	0.567804000	-1.349365000
1	0.835507000	-0.916575000	-1.207938000
1	2.307079000	-1.512727000	-1.996013000
1	2.306887000	2.483981000	-0.312633000
1	0.835024000	1.504155000	-0.189357000
1	2.040397000	0.971513000	-2.308272000
1	3.514493000	0.587815000	-1.396332000

Cyclohexane Parallel displaced Dimer-B

Atomic number	X	Y	Z
1	-3.622459000	1.195723000	-1.071511000
6	-2.608025000	1.353902000	-0.658726000
6	-2.621892000	1.036753000	0.845355000
6	-1.614377000	0.446531000	-1.401627000
1	-2.355400000	2.415139000	-0.825054000
6	-2.942173000	-0.446344000	1.091617000
1	-3.353619000	1.678496000	1.365419000
1	-1.629843000	1.269574000	1.275322000
6	-1.932207000	-1.036884000	-1.155170000
1	-1.626291000	0.667177000	-2.482940000
1	-0.591766000	0.662024000	-1.041833000
6	-1.947927000	-1.353339000	0.348949000
1	-2.928221000	-0.667453000	2.172644000
1	-3.966765000	-0.659877000	0.732257000
1	-2.924707000	-1.270571000	-1.585313000
1	-1.200876000	-1.679225000	-1.675605000
1	-2.199370000	-2.415122000	0.514103000
1	-0.935716000	-1.196036000	0.763979000
1	1.628798000	1.269284000	-1.274360000
6	2.621342000	1.036646000	-0.845436000
6	2.608815000	1.353572000	0.658694000
6	2.941416000	-0.446442000	-1.092061000

1	3.352488000	1.678507000	-1.366159000
6	1.615445000	0.446386000	1.402217000
1	2.356630000	2.414845000	0.825453000
1	3.623540000	1.195010000	1.070615000
6	1.947318000	-1.353299000	-0.349017000
1	2.926874000	-0.667443000	-2.173101000
1	3.966164000	-0.660124000	-0.733236000
6	1.932343000	-1.037118000	1.155165000
1	0.592588000	0.662541000	1.043508000
1	1.628468000	0.666727000	2.483582000
1	2.198360000	-2.415137000	-0.514431000
1	0.935018000	-1.195604000	-0.763658000
1	1.200781000	-1.679129000	1.675683000
1	2.924857000	-1.271511000	1.584877000

Cyclohexane T-shaped Dimer-C

Atomic number	X	Y	Z
6	-2.514700000	1.520284000	0.254639000
6	-1.309281000	0.680358000	-0.195514000
6	-1.451134000	-0.777657000	0.268541000
6	-2.766406000	-1.388819000	-0.239234000
6	-3.972846000	-0.549565000	0.210357000
6	-3.830483000	0.909046000	-0.252536000
1	-0.592275000	-1.376622000	-0.077431000
1	-1.242385000	0.703685000	-1.300005000
1	-0.372973000	1.117254000	0.190440000
1	-2.534713000	1.558893000	1.360138000
1	-2.411085000	2.559457000	-0.101790000
1	-2.742885000	-1.427862000	-1.344703000
1	-2.867280000	-2.428254000	0.117142000
1	-4.909386000	-0.985238000	-0.178093000
1	-4.039755000	-0.574553000	1.314474000
1	-3.841916000	0.941178000	-1.358439000
1	-4.690218000	1.507262000	0.095001000
1	-1.439219000	-0.808296000	1.374624000
6	2.186420000	-0.675392000	1.264611000
6	3.136591000	0.532761000	1.253647000
6	2.351736000	-1.518512000	-0.010191000
1	2.366300000	-1.296489000	2.158940000
1	1.143391000	-0.316351000	1.329063000
6	2.922353000	1.387854000	-0.005536000
1	2.990964000	1.142526000	2.161838000

1	4.182785000	0.172711000	1.272193000
6	2.147063000	-0.662923000	-1.270997000
1	1.645940000	-2.367276000	-0.002270000
1	3.370230000	-1.951010000	-0.028288000
6	3.099323000	0.543666000	-1.277736000
1	1.899359000	1.808380000	0.010446000
1	3.620044000	2.242787000	-0.011999000
1	1.104406000	-0.297916000	-1.298943000
1	2.297214000	-1.275098000	-2.176870000
1	2.927583000	1.161555000	-2.175772000
1	4.144056000	0.182665000	-1.330006000

Table S3. The results of NBO analysis of Donor-Acceptor orbital σ-stacking interactions, their E_2 energies calculated at MP2 level of theory with aug-cc-pVDZ basis set. The category of interaction is also indicated.

Donor-Acceptor orbital interaction	**E_2 energy (kcal/mol)**	**Category of interaction**
Dimer A		
σ(C3-H8)→σ*(C24-H31)	0.41	Axial-axial
σ(C3-H8)→σ*(C27-H34)	0.41	Axial-axial
σ(C4-H11)→σ*(C20-H19)	0.41	Axial-axial
σ(C4-H11)→σ*(C24-H31)	0.41	Axial-axial
σ(C12-H18)→σ*(C20-H19)	0.41	Axial-axial
σ(C4-H11)→σ*(C27-H34)	0.42	Axial-axial
σ(C20-H19)→σ*(C4-H11)	0.41	Axial-axial
σ(C20-H19)→σ*(C12-H18)	0.41	Axial-axial
σ(C24-H31)→σ*(C3-H8)	0.41	Axial-axial
σ(C24-H31)→σ*(C4-H11)	0.41	Axial-axial
σ(C27-H34)→σ*(C3-H8)	0.40	Axial-axial
σ(C27-H34)→σ*(C12-H18)	0.42	Axial-axial
Dimer B		
σ(C3-H8)→σ*(C24-H31)	0.54	Axial-axial
σ(C4-H11)→σ*(C20-H19)	0.41	Axial-axial
σ(C4-H11)→σ*(C24-H31)	0.33	Axial-axial
σ(C4-H11)→σ*(C27-H34)	0.18	Axial-axial
σ(C9-H16)→σ*(C27-H34)	0.35	Axial-axial
σ(C12-H8)→σ*(C24-H31)	0.22	Axial-axial
σ(C12-H8)→σ*(C27-H34)	0.12	Axial-axial
σ(C12-H8)→σ*(C30-H35)	0.08	Axial-equatorial
σ(C20-H19)→σ*(C4-H11)	0.54	Axial-axial
σ(C24-H31)→σ*(C3-H8)	0.40	Axial-axial
σ(C24-H31)→σ*(C4-H11)	0.33	Axial-axial
σ(C24-H31)→σ*(C12-H18)	0.18	Axial-axial
σ(C27-H34)→σ*(C4-H11)	0.22	Axial-axial
σ(C27-H34)→σ*(C9-H16)	0.08	Axial-equatorial
σ(C27-H34)→σ*(C12-H18)	0.12	Axial-axial
σ(C30-H35)→σ*(C12-H18)	0.35	Equatorial-axial
Dimer C		
σ(C2-H8)→σ*(C27-H33)	0.21	Axial-equatorial
σ(C2-H9)→σ*(C19-H23)	0.24	Equatorial-axial
σ(C2-H9)→σ*(C24-H31)	0.32	Equatorial-axial
σ(C2-H9)→σ*(C27-H33)	0.09	Equatorial-axial
σ(C3-H7)→σ*(C19-H23)	0.08	Equatorial-axial
σ(C3-H7)→σ*(C21-H28)	0.05	Equatorial- equatorial

σ(C3-H7)→σ*(C27-H33)	0.15	Equatorial-axial
σ(C3-H18)→σ*(C19-H23)	0.12	Axial-equatorial
σ(C19-H23)→σ*(C2-H9)	0.16	Axial-equatorial
σ(C19-H23)→σ*(C3-C4)	0.12	---
σ(C21-H28)→σ*(C3-H7)	0.22	Equatorial- equatorial
σ(C24-H31)→σ*(C2-H9)	0.34	Axial-equatorial
σ(C27-H33)→σ*(C1-C2)	0.14	--
σ(C27-H33)→σ*(C3-H7)	0.11	Axial-equatorial

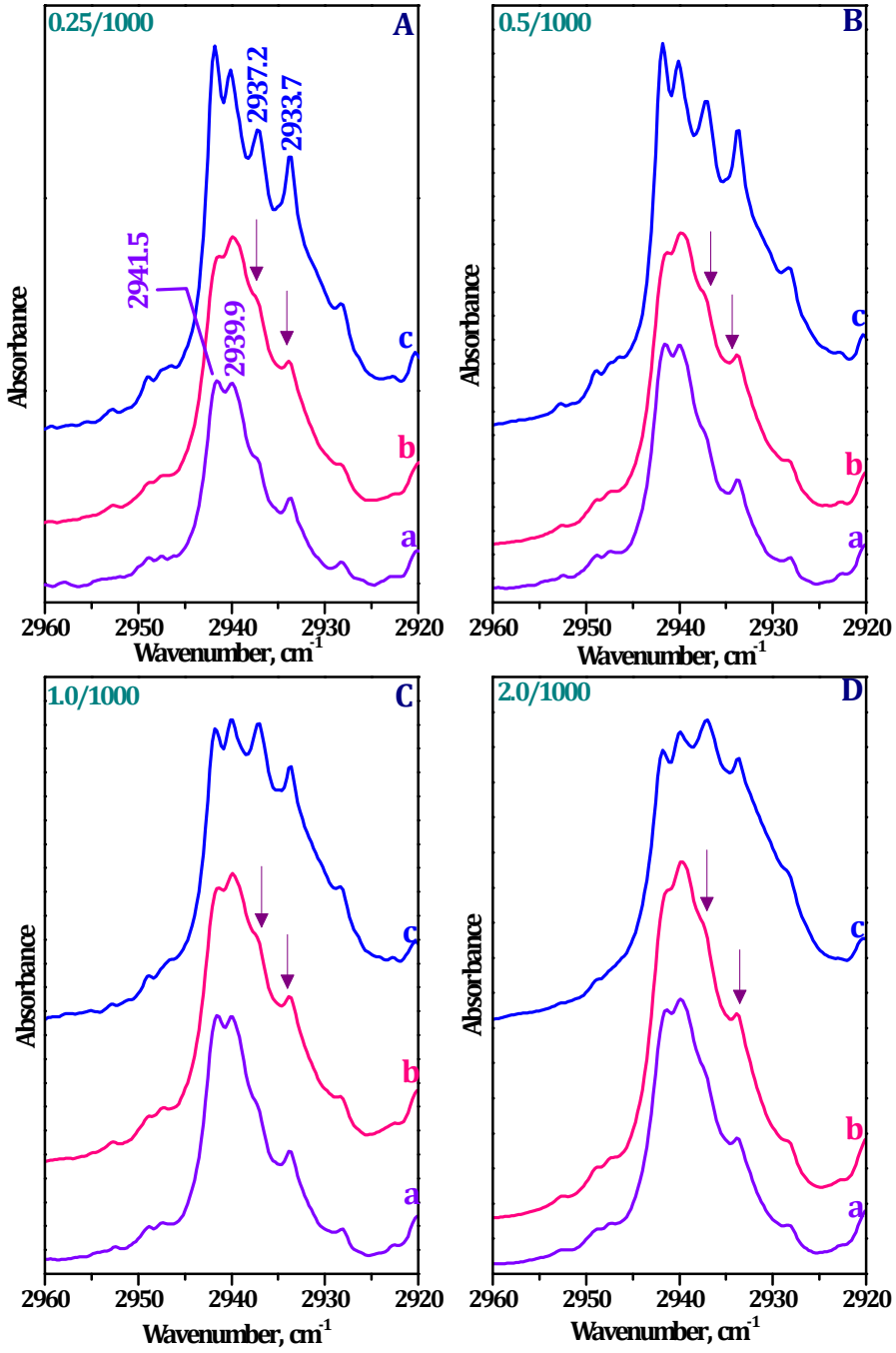
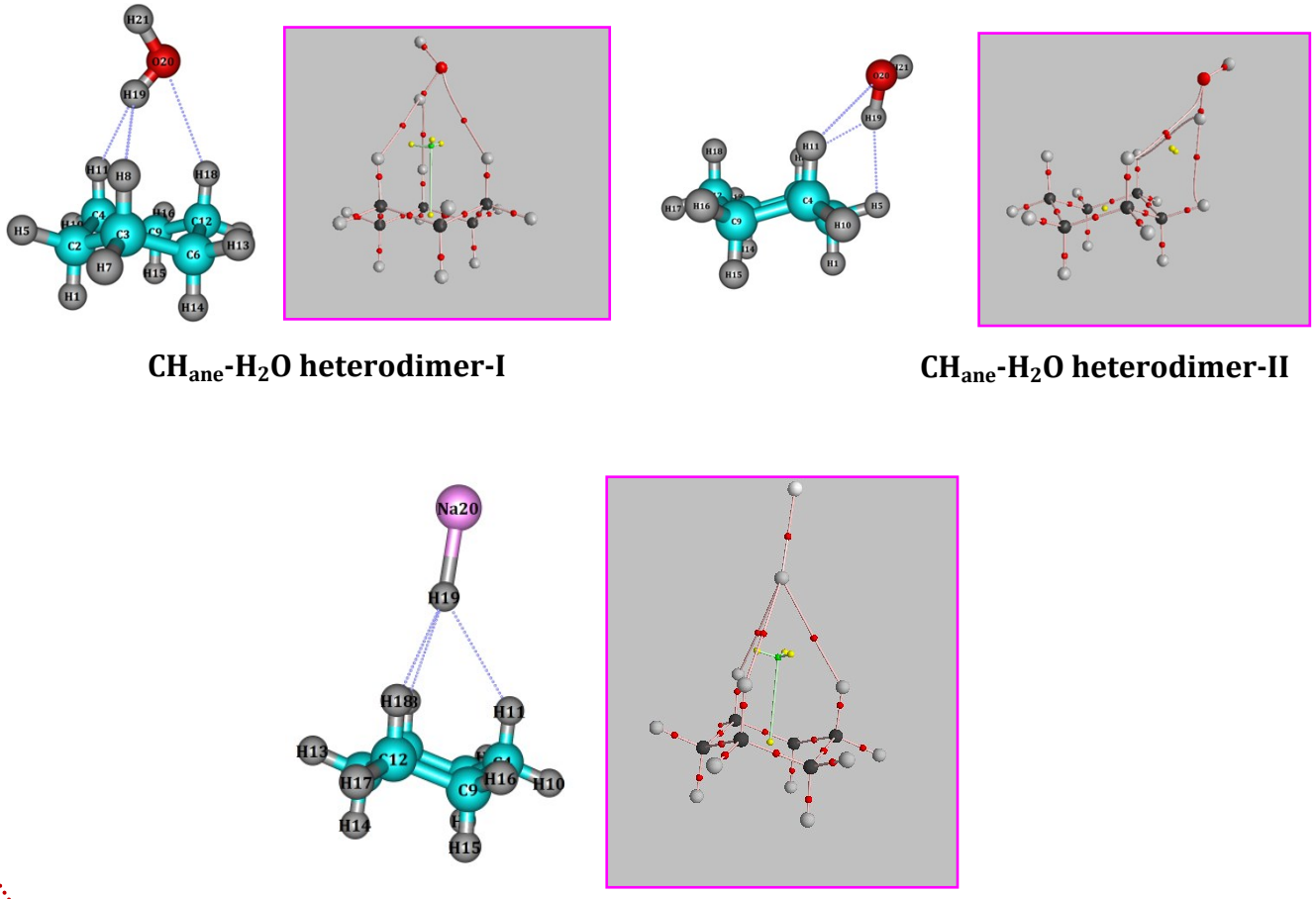


Figure S1. The infrared spectra of matrix isolated cyclohexane in N_2 matrix. Grids 'A' to 'D' indicate the increase of concentration of cyclohexane in N_2 matrix. The infrared spectra a) recorded at 10 K; b) recorded at 10 K after supersonic expansion; c) recorded at 10 K after annealing the matrix at 32 K for 15 minutes through supersonic expansion of cyclohexane in N_2 matrix.



CH_{ane}-H_2O heterodimer-I **CH_{ane}-H_2O heterodimer-II**

CH_{ane}-NaH heterodimer

Figure S2. The structures of CH_{ane}-H_2O heterodimers and CH_{ane}-NaH heterodimer calculated at MP2 level of theory using aug-cc-pVDZ basis set.