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

Supporting Information

Many-Body Energy Decomposition Analysis (MB-EDA) Scheme based on Target State Optimization Self-Consistent Field (TSO-SCF) Method

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S1. Additional Figures on Interactions

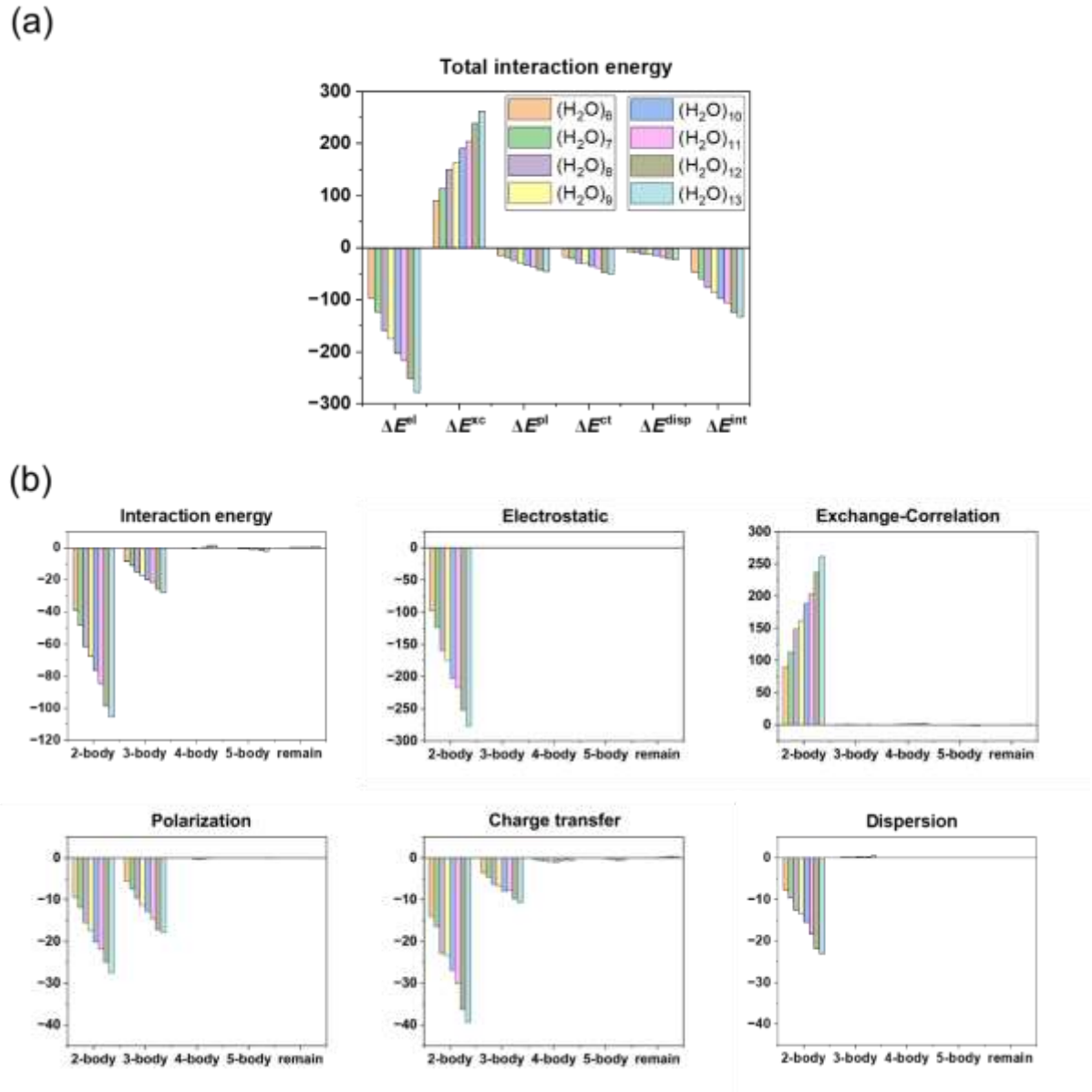

Figure S1. (a) EDA and (b) MB-EDA results of water clusters with 6-13 monomers. Computational method is B3LYP-D3(BJ)/6-31+G(d), energy unit is kcal/mol.

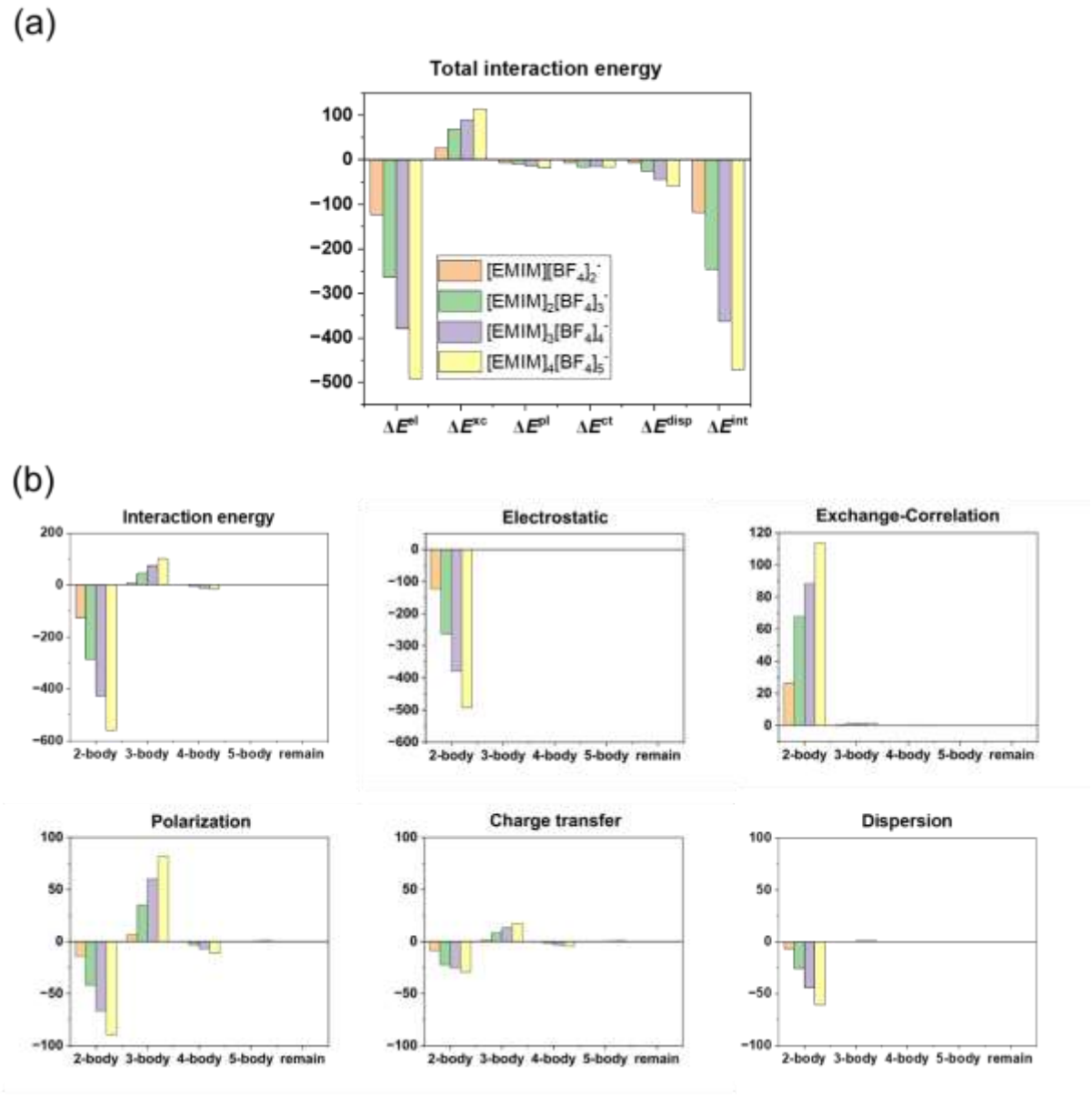

Figure S2. (a) EDA and (b) MB-EDA results of $[EMIM]_m[BF_4]_{m+1}^-$ (m = 1~4) clusters. Computational method is B3LYP-D3(BJ)/def2-SVP, energy unit is kcal/mol.

S2. Many-Body Polarization Effects

In the optimized target state Ψ_S^{TSO}, the total charge of each monomer remains unchanged, the charge within a monomer is redistributed due to the polarization effect of the presence of other monomers. The change in the charge of an atom or group within monomer will reflect the polarization effect.

In the optimized supermolecule state Ψ_S^S, the total charge of each monomer no longer remains constant, the charge of the entire system will be redistributed. Transferred charge of a monomer is the change in its total charge from Ψ_S^{TSO} to Ψ_S^S state.

In many-body expansion formalism for a cluster system of N monomers, the charge population for different expanding order is different. According to Eq. (13) in the main text, there are $\binom{N}{n}$ combination

ways for n-body sub-system, and each subsystem has a different electronic density population. Therefore, we should use an average approach to analyze the charge changes of the cluster system when it is truncated to n-body order in MBE.

In the *n*-body summation term of MBE according to Eq. (13), a specified monomer A will appear $\binom{N-1}{n-1}$ times, and each of the other monomers will appear $\binom{N-2}{n-2}$ times in these $\binom{N-1}{n-1}$ sub-terms. Therefore, the average influence of the other monomers on monomer A can be expressed as:

$$\overline{\Delta\rho} = \frac{\sum_{i=1}^{\binom{N-1}{n-1}} \Delta\rho}{\binom{N-2}{n-2}} \qquad (S1)$$

Where $\Delta\rho$ can be the charge difference of an atom or group within monomer A from Ψ_S^0 to Ψ_S^{TSO} state, which can be used as an indicator of polarization effect, or the transferred charge of monomer A from Ψ_S^{TSO} to Ψ_S^S state, which directly reflects charge transfer effects, as mentioned above.

Mulliken charges are used in the following calculations.

Table S1. Illustration for many-body polarization effect of four water hexamer clusters in optimized target state Ψ_S^{TSO}. Average changes of the Mulliken charges for each atom within the selected monomer which has the most negative oxygen atom are shown. Computational method is B3LYP-D3(BJ)/aug-cc-pVTZ.

		Origin*	2-body	3-body	4-body	5-body	6-body
Cage	O	-0.368612	-0.201011	-0.210844	-0.220407	-0.229589	-0.238099
	H1	0.180715	0.076052	0.082358	0.088663	0.095067	0.101379
	H2	0.187896	0.124959	0.128485	0.131744	0.134523	0.136720
Prism	O	-0.371207	-0.192062	-0.199021	-0.205937	-0.212204	-0.217531
	H1	0.191381	0.134018	0.137890	0.141596	0.144998	0.147995
	H2	0.179826	0.058043	0.061131	0.064342	0.067206	0.069536
Book	O	-0.370519	-0.161903	-0.162340	-0.162940	-0.163382	-0.163567
	H1	0.198075	0.180862	0.182289	0.183916	0.185562	0.187109
	H2	0.172444	-0.018958	-0.019949	-0.020976	-0.022180	-0.023541
Ring	O	-0.365335	-0.131745	-0.130286	-0.128550	-0.126476	-0.123749
	H1	0.171362	-0.018267	-0.019058	-0.019993	-0.021214	-0.022737
	H2	0.193973	0.150012	0.149345	0.148543	0.147689	0.146485

*The Mulliken charges of isolated monomer.

Table S2. The numbers of transferred Mulliken charges for each monomer of four water hexamer clusters in

optimized super-molecular state Ψ_S^S. Computational method is B3LYP-D3(BJ)/aug-cc-pVTZ.

	Monomer 1	Monomer 2	Monomer 3	Monomer 4	Monomer 5	Monomer 6
Cage	-0.053574*	0.050323	-0.020299	0.040760	0.006662	-0.023872
Prism	-0.042048	-0.052243*	0.026748	0.058479	0.033438	-0.024374
Book	-0.056478*	0.023733	0.009581	0.005499	0.010681	0.006985
Ring	-0.000893	-0.000002	-0.000002	-0.000894*	0.000896	0.000895

*The monomer will be selected for further analysis in Table S3.

Table S3. Illustration for many-body charge transfer effect of four water hexamer clusters in optimized super-molecular state Ψ_S^S. The numbers of average transferred Mulliken charges for the selected monomer which has the most negative transferred charge value are shown. Computational method is B3LYP-D3(BJ)/aug-cc-pVTZ.

	2-body	3-body	4-body	5-body	6-body
Cage	-0.032416	-0.039896	-0.044993	-0.049595	-0.053574
Prism	-0.016368	-0.022859	-0.029974	-0.039111	-0.052243
Book	-0.025302	-0.032875	-0.039727	-0.047222	-0.056478
Ring	-0.000381	-0.000492	-0.000672	-0.000781	-0.000894

Table S4. The numbers of the transferred Mulliken charges for each monomer of $[EMIM]_m[BF_4]_{m+1}^-$ (m = 1~4) cluster systems in optimized super-molecular state Ψ_S^S. Negative electronic charges transfer from BF_4^- to $EMIM^+$. Computational method is B3LYP-D3(BJ)/def2-SVP.

	$[EMIM]_1[BF_4]_2^-$	$[EMIM]_2[BF_4]_3^-$	$[EMIM]_3[BF_4]_4^-$	$[EMIM]_4[BF_4]_5^-$
Monomer 1	-0.340164	-0.395163	-0.364125	-0.354157
Monomer 2	0.145699	-0.394497	-0.347297	-0.288923
Monomer 3	0.194466*	0.248137	-0.374148	-0.342143
Monomer 4	-	0.263577	0.256138	-0.364230
Monomer 5	-	0.277945*	0.286008	0.248145
Monomer 6	-	-	0.306012*	0.228512
Monomer 7	-	-	0.237411	0.310201
Monomer 8	-	-	-	0.325146
Monomer 9	-	-	-	0.325146*

*The monomer will be selected for further analysis in Table S5.

Table S5. Illustration for many-body charge transfer effect of $[EMIM]_m[BF_4]_{m+1}^-$ (m = 1~4) cluster systems in optimized super-molecular state Ψ_S^S. The monomer BF_4^- with the most positive transferred charge value was selected for analysis. Computational method is B3LYP-D3(BJ)/aug-cc-pVTZ.

	2-body	3-body	4-body	5-body	N-body
$[EMIM]_1[BF_4]_2^-$	0.210621	0.194466	-	-	-
$[EMIM]_2[BF_4]_3^-$	0.350414	0.320941	0.297064	0.277945	-
$[EMIM]_3[BF_4]_4^-$	0.405559	0.377495	0.354336	0.335171	0.306012
$[EMIM]_4[BF_4]_5^-$	0.478056	0.447191	0.420229	0.396537	0.325146

Table S6. Illustration for many-body polarization effect of $(CH_4)_m(CH_3CN)_{6-m}$ (m= 0,1,3,5) cluster systems in optimized target state Ψ_S^{TSO}. The numbers of average transferred Mulliken charges $\overline{\Delta\rho}^C(CH_3CN)$ for the most positive central carbon atom of CH_3CN are shown. Computational method is B3LYP-D3(BJ)/aug-cc-pVDZ.

	Origin*	2-body	3-body	4-body	5-body	6-body
$(CH_4)_5(CH_3CN)$	1.004001	0.052402	0.054552	0.056918	0.059249	0.061545
$(CH_4)_3(CH_3CN)_3$	1.000341	0.085728	0.090324	0.093924	0.097625	0.101412
$(CH_4)(CH_3CN)_5$	0.997286	0.108682	0.110904	0.112288	0.113787	0.115425
$(CH_3CN)_6$	0.999899	0.106939	0.108314	0.109903	0.111696	0.113590

*The Mulliken charges of central carbon atom in independent CH_3CN monomer.

Table S7. Illustration for many-body polarization effect of $(CH_4)_m(CH_3CN)_{6-m}$ (m = 1,3,5,6) cluster systems in optimized target state Ψ_S^{TSO}. The numbers of average transferred Mulliken charges $\overline{\Delta\rho}^C(CH_4)$ for the most positive central carbon atom of CH_4 are shown. Computational method is B3LYP-D3(BJ)/aug-cc-pVDZ.

	Origin*	2-body	3-body	4-body	5-body	6-body
$(CH_4)(CH_3CN)_5$	1.246166	0.111356	0.109147	0.107261	0.105475	0.103704
$(CH_4)_3(CH_3CN)_3$	1.247238	0.140870	0.139586	0.138405	0.137277	0.136136
$(CH_4)_5(CH_3CN)$	1.247395	0.162999	0.163967	0.161859	0.165865	0.166715
$(CH_4)_6$	1.249296	0.131034	0.130665	0.130402	0.130140	0.129367

* The Mulliken charges of central carbon atom in independent CH_4 monomer.

S3. Kinetic Stability of Acetonitrile-Methane Clusters

To explore the kinetic stability of acetonitrile-methane clusters $(CH_4)_m(CH_3CN)_{6-m}$, we performed NVT ab initio molecular dynamics (AIMD) simulations for 3 ones: $(CH_4)_6$, $(CH_4)_3(CH_3CN)_3$, and $(CH_3CN)_6$. The forces were evaluated at B3LYP-D3(BJ)/def2-SVP level of theory. Temperature was controlled at 298.15 K with Nosé–Hoover chain algorithm with chain length and time constant to be 5 and 0.5 ps, respectively. The time step of AIMD was 0.5 fs, and equation-of-motion was integrated for 1 ps.

For $(CH_4)_6$, the cluster disintegrates in less than 200 fs (Figure S3(a)), since they are only loosely bound by weak dispersion interactions. In contrast, for $(CH_3CN)_6$, the cluster keeps bound in 1 ps and exhibits only smale vibrations (Figure S3(c)), resulting from their strong dipole-dipole interactions. For $(CH_4)_3(CH_3CN)_3$, the cluster experiences large deformation but is still bound within 1 ps (Figure S3(b)). The different kinetic stabilities of these clusters are in line with their interaction strengths.

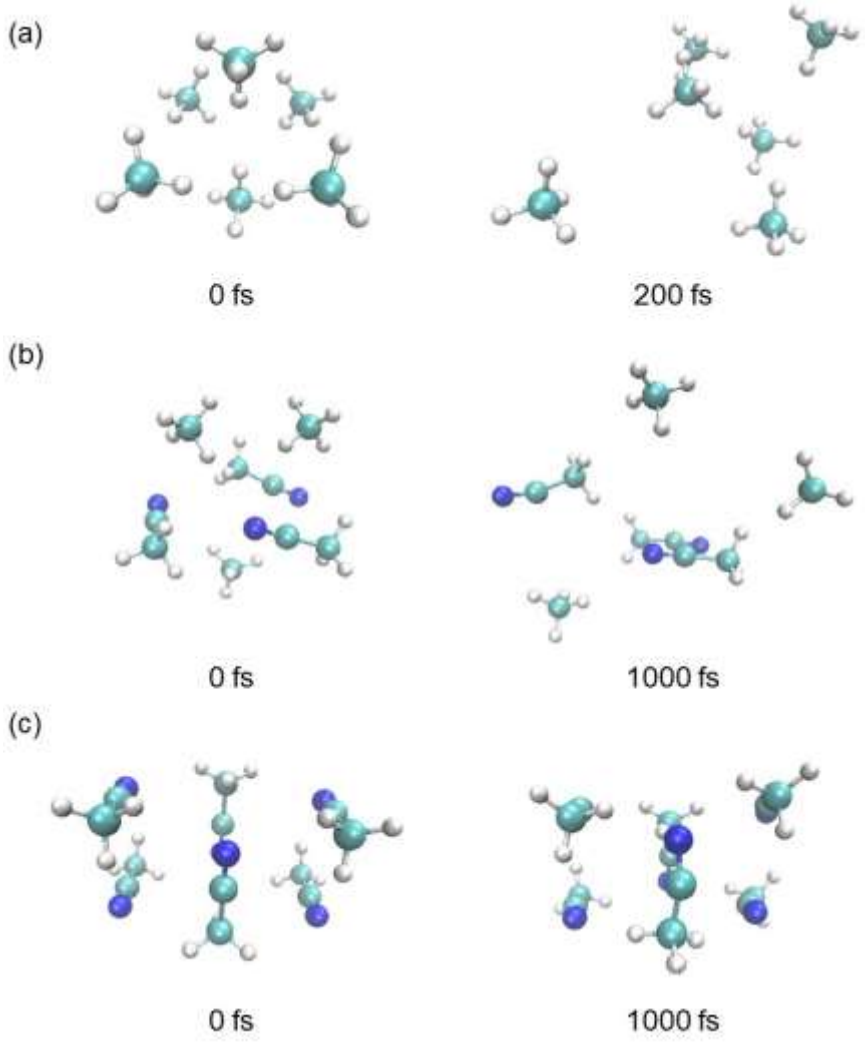

Figure S3. The geometry snapshots of NVT AIMD simulations of (a) $(CH_4)_6$, (b) $(CH_4)_3(CH_3CN)_3$, and (c) $(CH_3CN)_6$ clusters.

S4. Geometries of Acetonitrile-Methane Clusters

Below are the geometries of acetonitrile-methane clusters $(CH_4)_m(CH_3CN)_{6-m}$ (m = 0,1,3,5,6) predicted with ABCluster (http://zhjun-sci.com/abcluster).

$(CH_3CN)_6$

C	0.61031825	-0.09202876	5.07813859
H	-0.05543391	-0.85301403	5.42824667
H	0.27941647	0.86189891	5.43229266
H	1.59708745	-0.28556542	5.44382862
C	0.62454489	-0.09117346	3.53820454
N	0.63513728	-0.09053666	2.39165365
C	5.25881476	5.62742404	1.41860485
H	5.58974625	4.67358629	1.06423486
H	5.92444410	6.38852842	1.06852371
H	4.27197137	5.82093671	1.05310238
C	5.24482891	5.62630241	2.95854093
N	5.23441580	5.62546730	4.10509334
C	-0.72781204	3.05897554	1.39672408
H	-1.73586184	3.10197472	1.04051229
H	-0.26248494	2.16270823	1.04306509
H	-0.18574177	3.90831214	1.03660429
C	-0.72687300	3.06463404	2.93671340
N	-0.72617385	3.06884705	4.08330545
C	2.21139789	4.43908885	5.00090932
H	2.87447903	5.10506800	5.51247101
H	1.26872516	4.41616465	5.50661843
H	2.06911335	4.77926939	3.99645355
C	2.81858522	3.02396222	4.98246524
N	3.27066379	1.97033613	4.96873279
C	6.59786117	2.47590029	5.09931852
H	6.13276214	3.37218000	5.45324756
H	7.60601580	2.43271879	5.45520993
H	6.05579220	1.62658433	5.45948894

C	6.59644116	2.47045667	3.55932880
N	6.59538390	2.46640364	2.41273645
C	3.65821725	1.09534952	1.49551345
H	3.80052580	0.75516045	2.49996347
H	4.60085922	1.11815319	0.98974156
H	2.99502119	0.42944749	0.98400142
C	3.05120504	2.51055092	1.51398469
N	2.59925685	3.56423268	1.52773736

$(CH_4)(CH_3CN)_5$

C	1.78408557	2.36735764	1.55417874
H	1.15991689	2.79344940	0.77104865
H	1.39850584	1.38860358	1.83310928
H	2.80431908	2.26486618	1.18941507
H	1.77360044	3.02251139	2.42314198
C	-1.35787715	3.11871359	3.80066207
H	-2.29295069	2.61025537	3.69108151
H	-0.98388755	3.38952838	2.83542106
H	-1.49857912	4.00121848	4.38912376
C	-0.34782825	2.19059348	4.50065799
N	0.40419906	1.49956586	5.02183676
C	6.81177778	4.47074424	6.39933179
H	6.50496704	4.63035264	5.38676450
H	7.85899361	4.25256260	6.42452859
H	6.61712839	5.35200974	6.97412029
C	6.02629616	3.28668028	6.99314249
N	5.44146939	2.40509083	7.43526155
C	2.18933876	3.93746385	6.94275895
H	1.93437158	3.58712341	5.96441673
H	1.29828951	4.21752646	7.46476973
H	2.68860200	3.15931121	7.48138105
C	3.12018153	5.15857169	6.82432169
N	3.81323629	6.06774198	6.73613976

C	3.42827111	6.37013050	3.14975154
H	3.89135880	5.70162547	2.45437323
H	4.05475317	6.47995561	4.01019199
H	3.28722968	7.32456702	2.68708824
C	2.06309696	5.80053581	3.57807552
N	1.04666275	5.37644668	3.89698219
C	3.68570246	0.89992217	4.81173923
H	4.52237877	0.23394066	4.84836659
H	2.93714892	0.49681985	4.16206608
H	3.27950079	1.01671065	5.79472435
C	4.14349912	2.27051804	4.27930221
N	4.48434954	3.29098896	3.88287864

$(CH_4)_3(CH_3CN)_3$

C	11.83673120	8.75849834	7.37638800
H	11.52995368	9.49054623	8.12098648
H	11.48221522	9.06855826	6.39525868
H	12.92262494	8.68701033	7.36382993
H	11.41213094	7.78787853	7.62547690
C	8.77383090	4.35309609	4.16896521
H	9.60239866	3.65873221	4.04339553
H	7.87403716	3.92758838	3.72879720
H	8.60875168	4.53290660	5.22955490
H	9.01013611	5.29315715	3.67411320
C	14.19200474	5.53866884	7.45434383
H	14.76869258	6.30781709	6.94417173
H	13.18018145	5.89960087	7.62862855
H	14.15637496	4.64283954	6.83737232
H	14.66276997	5.30441786	8.40720271
C	12.14281610	6.38269002	4.33118617
H	13.07223259	6.90664815	4.25023531
H	11.64888826	6.67022585	5.23576205
H	11.52262351	6.62503933	3.49361405

C	12.40865216	4.86594078	4.35125960
N	12.60657919	3.73665203	4.36620518
C	8.07522075	7.49165656	6.82458951
H	8.76679329	7.61778655	7.63126097
H	7.75176715	6.47236740	6.78816877
H	7.22939010	8.12903206	6.97697738
C	8.76276975	7.85979447	5.49667730
N	9.27468123	8.13388989	4.50798629
C	11.25794449	2.64057684	7.21985246
H	10.91488442	2.22337462	6.29619004
H	10.88364141	2.05766971	8.03533733
H	12.32776394	2.63438040	7.23848152
C	10.75067000	4.08890751	7.34873558
N	10.37298109	5.16725553	7.44469492

$(CH_4)_5(CH_3CN)$

C	9.77734669	9.05533543	7.26217921
H	10.05655380	9.82102854	7.98342183
H	9.05133645	9.46402297	6.56195275
H	10.66195195	8.72924684	6.71851272
H	9.33954458	8.20704337	7.78482953
C	4.92846395	6.02991808	4.04138788
H	5.24791040	5.86353589	5.06837590
H	3.84449672	5.95320378	3.98169335
H	5.24012817	7.02213520	3.72075715
H	5.38132049	5.28079747	3.39472512
C	6.11603798	7.78460995	7.36544785
H	6.17484959	8.28244384	6.39945816
H	6.50361851	6.77161456	7.27569736
H	6.70706982	8.33591736	8.09426536
H	5.07861400	7.74846403	7.69237051
C	6.71617028	11.48050455	6.60989563
H	6.97776184	10.93523577	5.70508334

H	5.90135197	10.96914381	7.11883059
H	7.58178946	11.52808871	7.26782621
H	6.40377784	12.48954990	6.34784239
C	3.94619061	9.67991176	4.72576604
H	3.74438381	8.78710309	5.31449362
H	4.97661888	9.65869855	4.37619338
H	3.27358794	9.71032612	3.87071395
H	3.79017182	10.56351929	5.34166322
C	8.68856494	6.53797350	4.64021654
H	8.11851718	5.73924588	4.21362549
H	8.64265813	6.47847651	5.70757391
H	9.70709507	6.45878041	4.32205944
C	8.10915607	7.88715663	4.17589959
N	7.67775983	8.89168480	3.83019451

$(CH_4)_6$

C	2.19005710	2.29104709	5.68186921
H	1.17424371	1.90332038	5.72903503
H	2.16228594	3.37864326	5.65364138
H	2.74395993	1.96497210	6.56010620
H	2.67973883	1.91725263	4.78469421
C	4.32841774	1.13566675	1.65323371
H	5.21938840	0.53430616	1.82344003
H	3.81154601	1.29376120	2.59784116
H	4.61480492	2.09702064	1.23107906
H	3.66793163	0.61757901	0.96057459
C	1.26165977	-0.51430967	3.24740581
H	2.09130533	-0.97442045	2.71409560
H	1.43806715	-0.58054949	4.31928556
H	1.17919367	0.53137202	2.95726341
H	0.33807293	-1.03364075	2.99897867
C	5.52198329	3.49517021	4.35769825
H	4.60337243	3.71474851	3.81698305

H	5.27847142	3.13720947	5.35619690
H	6.08259886	2.72970006	3.82459500
H	6.12349044	4.39902282	4.43301806
C	1.45061933	3.53138314	2.18606477
H	1.54997168	2.74650172	1.43872032
H	1.07750157	4.43767510	1.71293531
H	0.75303121	3.21138035	2.95768806
H	2.42197287	3.72997539	2.63491541
C	4.69087959	-0.54538860	5.07392680
H	3.80476645	-0.53283801	5.70565415
H	5.47662900	-1.11838982	5.56249710
H	4.44813694	-1.00465778	4.11758937
H	5.03398598	0.47433123	4.90996659