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

Direct Chemical Dynamics Simulations of $CN^- + CH_3I$ Bimolecular Nucleophilic Substitution Reaction

SUPPORTING INFORMATION

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Product Energy Distributions

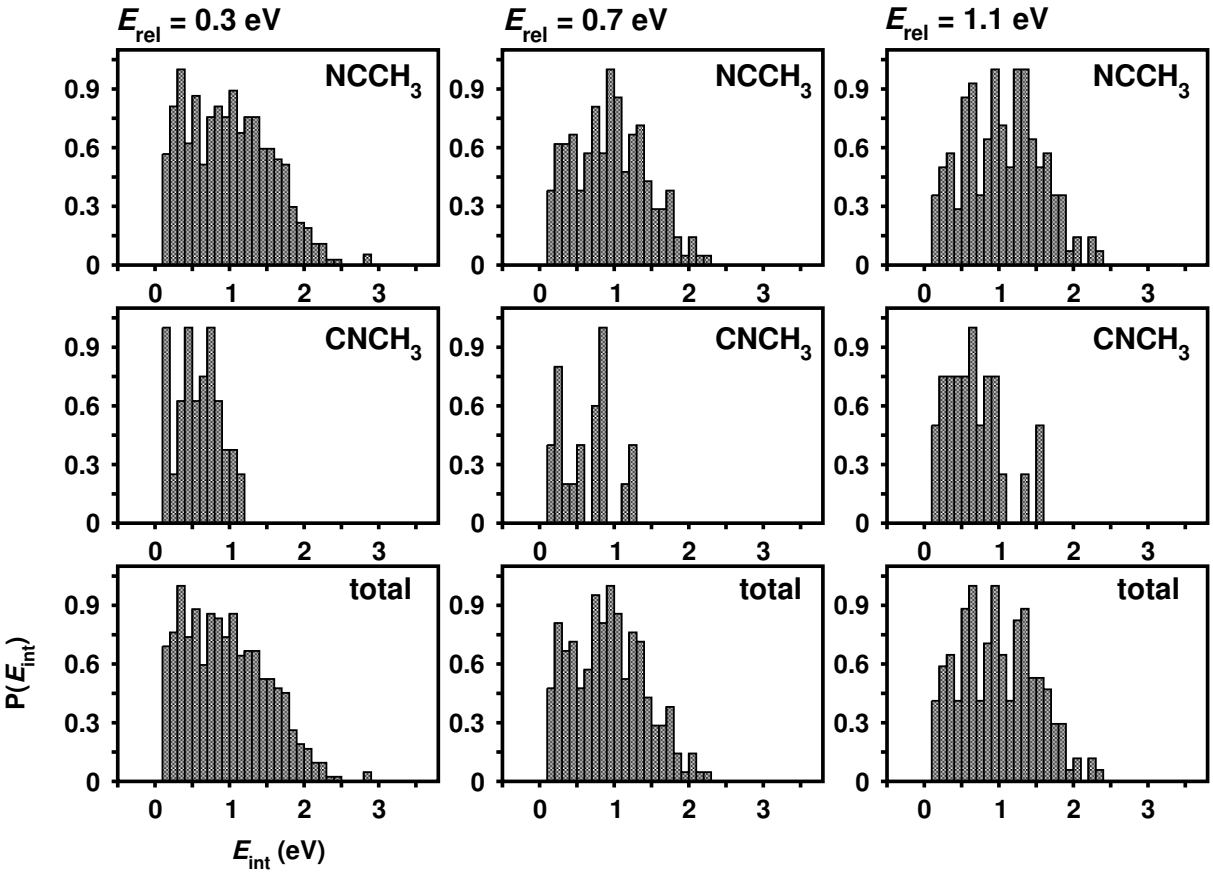


Figure S1: Product energy distributions for $NCCH_3$ (top row), $CNCH_3$ (middle row), and both isomers combined (bottom row) are given.

Isomerization Energy Profile

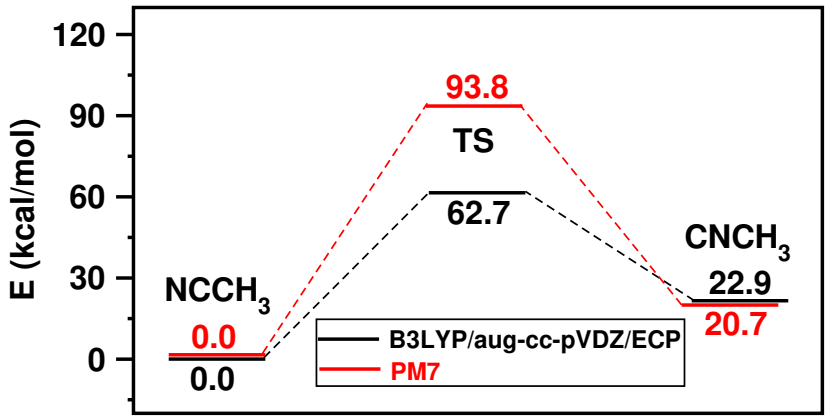


Figure S2: $NCCH_3 \rightleftharpoons CNCH_3$ isomerization energy profile computed using B3LYP/aug-cc-pVDZ/ECP (black) and semi-empirical (red) methods.

Table S1: Number of reactive trajectories as a function of impact parameter b at collision energies $E_{\mathrm{rel}} = 0.3$ and 1.1 eV. A total of 100 trajectories were generated at each b.

	0.3 eV		1.1 eV
b (Å)	reactivity	b (Å)	reactivity
0	9	0	2
1	5	1	5
2	5	2	6
3	4	3	0
4	4	4	1
total	27	total	14

Table S2: A comparison of stationary point energies (in kcal/mol) for CN^-+CH_3I reaction computed using B3LYP/aug-cc-pVDZ/ECP and Semiempirical method.

Stationary point	DFT (B3LYP)	SEMI-EM (PM7)
$CH_3I + CN^-/NC^-$	0	0
$CN^-\cdots HCH_2I$	-9.73	-8.82
$[CN\cdots H\cdots CH_2I]^{\dagger-}$	38.12	16.71
$HNC + CH_2I^-$	51.33	21.32
$[CN\cdots CH_3\cdots I]^{\dagger-}$	-5.63	-5.65
$CNCH_3\cdots I^-$	-38.22	-61.02
$CNCH_3 + I^-$	-27.76	-55.59
$NC^-\cdots CH_3I$	-10.05	-9.91
$NC^-\cdots HCH_2I$	-9.25	-9.41
$[NC\cdots H\cdots CH_2I]^{\dagger-}$	31.08	4.87
$HCN + CH_2I^-$	37.79	12.32
$[NC\cdots CH_3\cdots I]^{\dagger-}$	-8.84	-9.48
$NCCH_3\cdots I^-$	-60.88	-84.24
$NCCH_3 + I^-$	-50.61	-76.28

Trajectory Snapshots

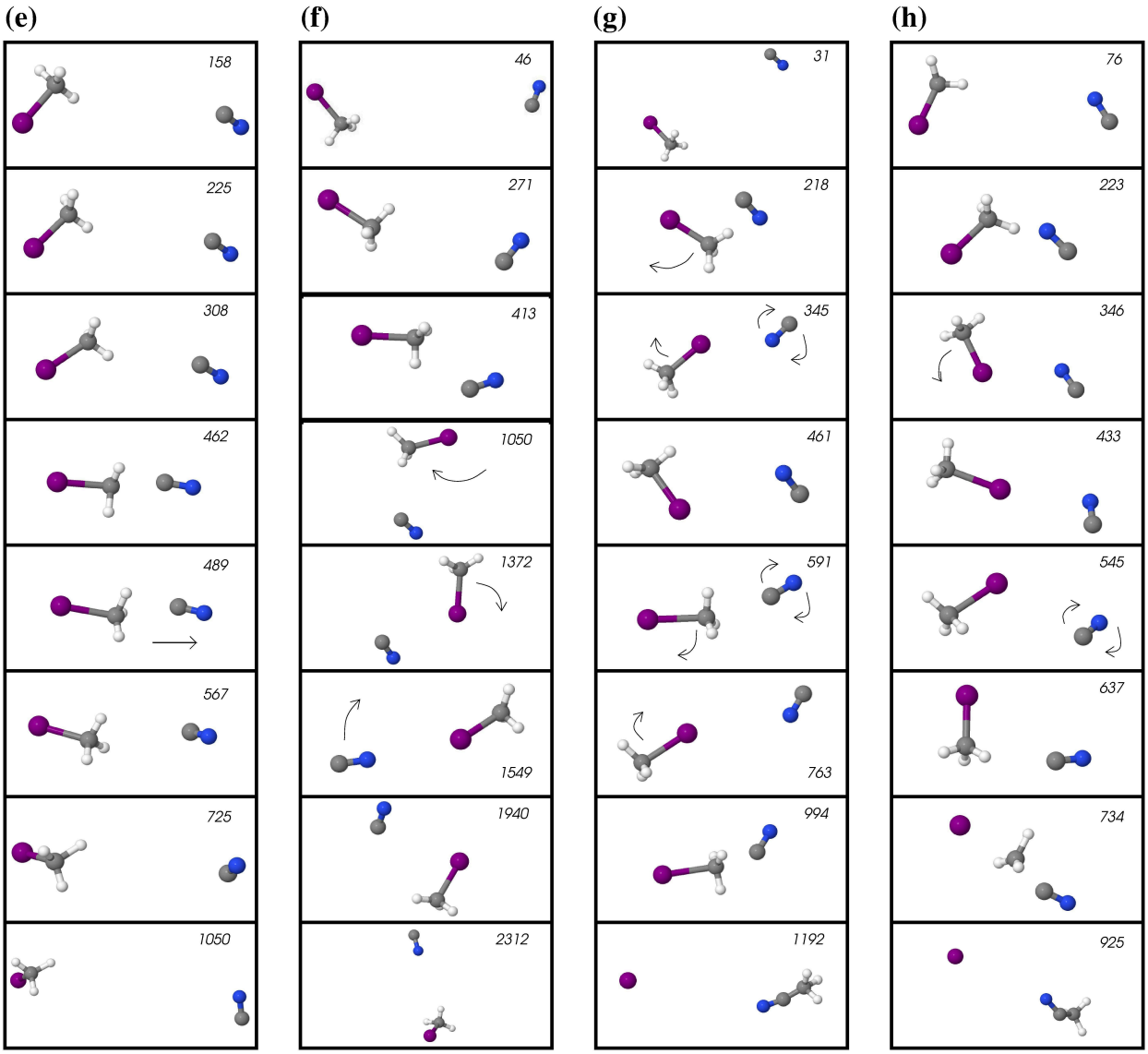


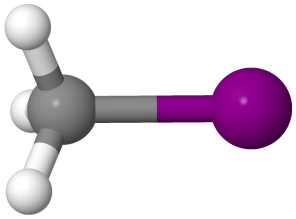
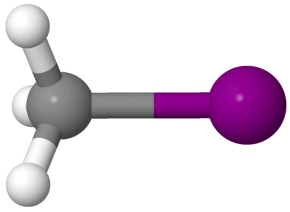
Figure S3: Trajectory snapshots for $CH_3I + CN^-$ reaction for DFT(e,f) and semiempirical (g,h) direct dynamics. **Unreacticve**: (e) Direct (f) Indirect mechanism. **Reactive**: (g,h) Direct roundabout mechanism.

Optimized Geometries

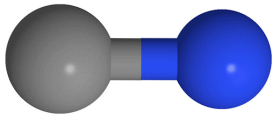
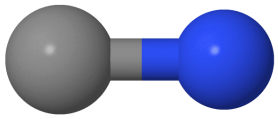
Stationary point geometries optimized using B3LYP/aug-cc-pVDZ/ECP and PM7 methods.

Coordinates are given in Angstrom units.

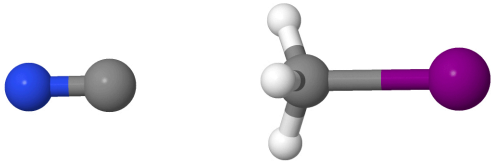
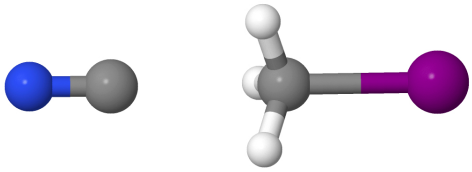
1. **CH_3I**

DFT	*PM7*
	
C 0.000000 0.000000 1.770758	C 0.621400 0.886300 -1.570500
H 0.726000 0.726000 2.133759	H 1.712700 0.886300 -1.570500
H 0.265734 -0.991734 2.133759	H 0.249700 1.912400 -1.570500
H -0.991734 0.265734 2.133759	H 0.249600 0.356000 -2.448900
I -0.000000 -0.000000 -0.321242	I -0.076400 -0.108900 0.193000

2. **CN^-**

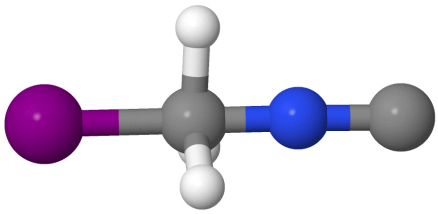
DFT	*PM7*
	
C 0.000000 0.000000 -0.623538	C -0.630200 0.000000 0.000000
N 0.000000 0.000000 0.534462	N 0.540400 0.000000 0.000000

3. $\mathbf{NC^{-}\cdots CH_3I}$

DFT	*PM7*
	
C 0.011109 -0.963580 0.000832	C -1.177500 -0.002200 -0.000300
I -0.001264 1.270245 -0.000058	I 1.026700 -0.002200 -0.000300
C -0.001301 -3.802293 0.000912	C -3.663100 0.003900 -0.000300
N -0.004318 -4.985000 -0.000886	N -4.828300 0.018900 0.003800
H -0.808982 -1.283323 0.639241	H -1.497600 0.459000 0.934400
H -0.130831 -1.276613 -1.031027	H -1.497800 0.576800 -0.867100
H 0.978208 -1.272803 0.390598	H -1.498200 -1.042100 -0.068300

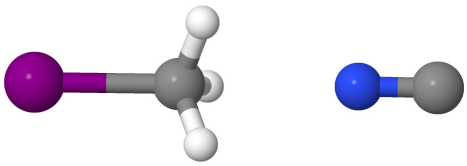
4. **$CN^{-}\cdots CH_3I$**

DFT



C	0.011322	0.893955	0.000066
N	0.018826	2.085718	0.000141
C	-0.022369	3.266549	-0.000160
I	-0.001911	-0.800983	-0.000012
H	0.673654	0.957558	0.849240
H	0.416545	0.959603	-0.997597
H	-1.054434	0.971904	0.148554

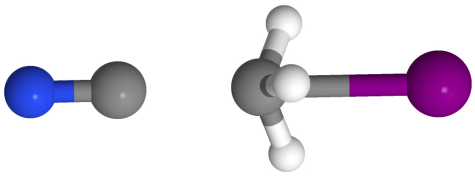
PM7



C	0.592801	0.025620	0.016500
N	3.262761	0.056829	0.004712
C	4.435193	0.063395	-0.011326
I	-1.563681	-0.001203	0.024542
H	0.951498	1.014953	0.313670
H	0.961749	-0.203699	-0.987027
H	0.974654	-0.720638	0.718701

5. **[NC···CH$_3$···I]$^{\dagger-}$**

DFT



C 0.010044 1.281602 0.000121

I -0.001094 -1.138373 -0.000031

C 0.001171 3.206122 0.001391

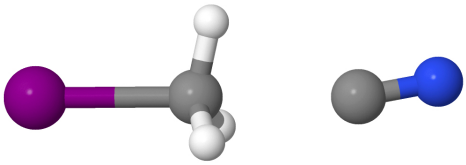
N -0.006314 4.381493 -0.000931

H 0.584832 0.913746 0.859202

H 0.469427 0.915384 -0.926499

H -1.019374 0.907865 0.066398

PM7



C 1.266600 -0.014400 -0.002000

C 3.578700 -0.014400 -0.002000

N 4.693700 0.317500 -0.002000

I -1.012700 -0.032000 0.000700

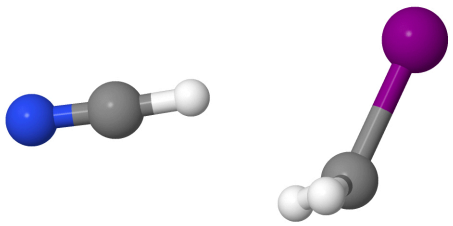
H 1.517900 -1.070000 0.058900

H 1.507900 0.460300 -0.949000

H 1.510300 0.567700 0.881500

6. $\mathbf{[NC\cdots H\cdots CH_2I]^{\dagger-}}$

DFT



C 1.491674 -0.323928 -0.031037

I -0.160288 1.034670 -0.004858

C -0.185558 -3.157253 0.112969

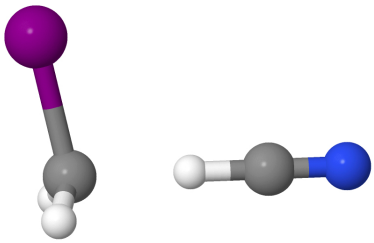
N -0.360330 -4.284814 -0.087421

H -0.065859 -2.143857 0.321668

H 1.738386 -0.785758 0.956139

H 1.508332 -1.027122 -0.899997

PM7



C -0.130000 0.290000 0.011000

I 1.965000 0.290000 0.011000

C -0.720000 3.143000 0.011000

N -0.955000 4.276000 0.014000

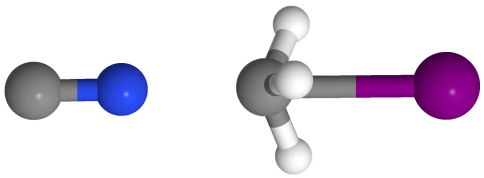
H -0.557000 0.001000 0.922000

H -0.560000 -0.016000 -0.893000

H -0.487000 2.018000 0.014000

7. $\mathbf{[CN{\cdots}CH_3{\cdots}I]^{\dagger-}}$

DFT



C 0.009793 1.297274 0.000089

I -0.001063 -1.122702 -0.000030

N 0.000690 3.221793 0.001258

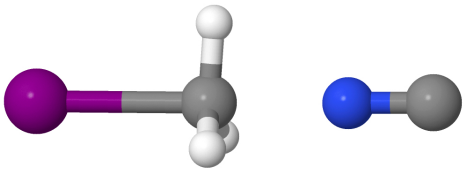
C -0.006923 4.397164 -0.001133

H 0.581064 0.929514 0.861552

H 0.473048 0.931081 -0.924611

H -1.019848 0.923420 0.062118

PM7



C -0.591184 0.946260 -1.561025

N 0.506022 0.907928 -3.131070

C 1.169133 0.895947 -4.080874

I -1.961904 1.011623 0.394666

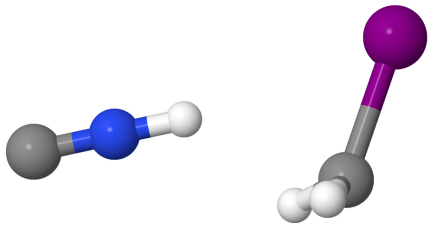
H -0.065343 1.874099 -1.317979

H -1.437745 0.970461 -2.252982

H -0.131060 -0.013534 -1.310669

8. **[CN···H···CH$_2$I]$^{\dagger-}$**

DFT



C 1.487571 -0.344566 -0.030583

I -0.158680 1.020947 -0.004444

N -0.201997 -3.171157 0.101026

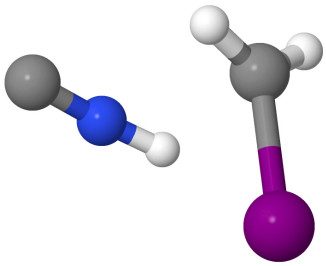
C -0.381052 -4.297376 -0.103096

H 1.729905 -0.810323 0.955834

H 1.503377 -1.045282 -0.901558

H -0.048369 -2.204848 0.276165

PM7



C 1.373000 -0.752000 0.072000

I -0.010000 0.794000 0.058000

N -0.776000 -3.421000 1.093000

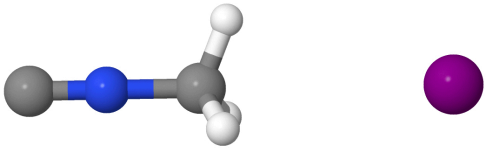
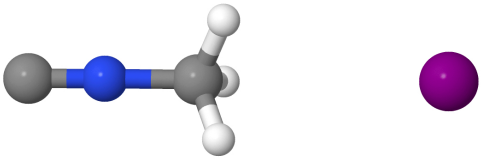
C -0.735000 -4.003000 0.070000

H 1.800000 -0.994000 0.979000

H 1.634000 -1.150000 -0.846000

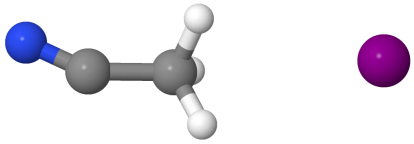
H -0.714000 -2.820000 1.845000

9. **$CNCH_3 \cdots I^-$**

DFT	*PM7*
	
C 0.002052 2.385868 0.000103	C -0.479202 -1.966555 -0.233958
N 0.002824 3.813845 0.000140	N 0.272163 -3.110156 0.174389
C -0.001402 4.987443 -0.000068	C 0.886132 -4.052944 0.508369
I 0.000065 -1.452315 0.000006	I -2.498692 1.107320 -1.331502
H -0.490692 2.032635 -0.915771	H -1.446704 -1.975159 0.285908
H -0.563850 2.032676 0.872710	H -0.651798 -2.025339 -1.317096
H 1.027430 1.970617 0.041567	H 0.046776 -1.020410 -0.002206

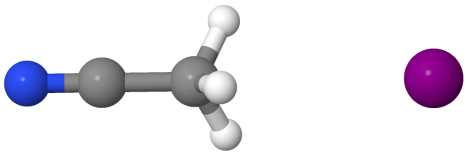
10. $\mathbf{NCCH_3 \cdots I^-}$

DFT



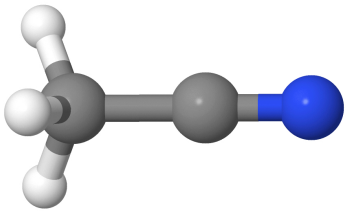
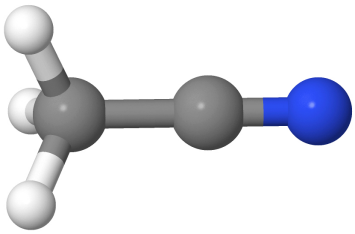
C	0.232579	2.218078 0.000000
C	0.230132	3.673354 0.000000
N	-0.320144	4.715552 0.000000
I	-0.022185	-1.393277 0.000000
H	-0.294101	1.852122 0.886736
H	1.228767	1.781988 0.000000
H	-0.294101	1.852122 -0.886736

PM7

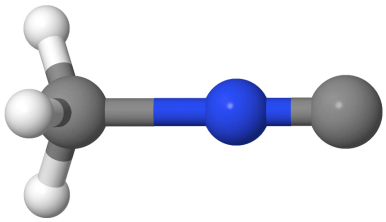
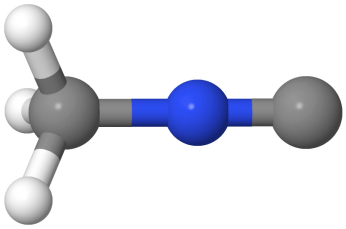


C	2.453700	-0.000600 -0.003400
C	3.884600	-0.000600 -0.003400
N	5.044100	-0.000300 -0.003400
I	-1.204600	0.000200 0.001100
H	2.013800	-0.799800 0.628900
H	2.014000	-0.148600 -1.011700
H	2.014200	0.946700 0.372700

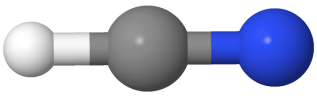
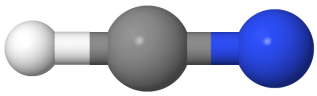
11. **CH_3CN**

DFT	*PM7*
	
C -0.002421 1.238362 0.000000	C -1.275100 0.000100 0.000000
C 0.000937 -0.224041 0.000000	C 0.162100 0.000100 0.000000
H 1.027794 1.617285 0.000000	H -1.688400 1.027200 0.000000
H -0.519279 1.612596 0.893218	H -1.688300 -0.513500 0.889600
H -0.519279 1.612596 -0.893218	H -1.688300 -0.513500 -0.889600
N 0.002331 -1.384471 0.000000	N 1.319000 -0.000200 -0.000000

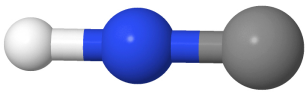
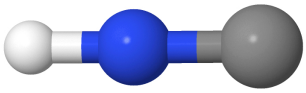
12. **CH_3NC**

DFT	*PM7*
	
C -0.002330 1.302951 0.000000	C -1.213900 0.000100 -0.000000
N 0.008183 -0.443788 0.000000	N 0.204500 0.000100 -0.000000
H 1.036771 1.639294 0.000000	H -1.609900 1.035600 -0.000000
H -0.524861 1.629895 0.901625	H -1.609600 -0.517800 0.896900
H -0.524861 1.629895 -0.901625	H -1.609600 -0.517800 -0.896900
C -0.005058 -1.601712 0.000000	C 1.380600 -0.000200 0.000000

13. **HCN**

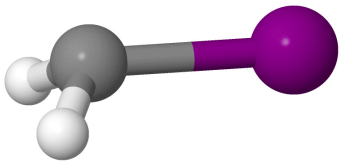
DFT	*PM7*
	
C 0.000000 0.000000 -0.502975	C 0.008000 0.011000 0.000000
N 0.000000 0.000000 0.654180	N 1.162000 0.011000 0.000000
H 0.000000 0.000000 -1.561407	H -1.036000 0.013000 0.000000

14. **HNC**

DFT	*PM7*
	
C 0.000000 0.000000 -0.732696	C -0.014208 0.028657 0.000000
N 0.000000 0.000000 0.424450	N 1.166180 0.028657 0.000000
H 0.000000 0.000000 1.425026	H 2.129370 0.032352 0.000000

15. $\mathbf{CH_2I^-}$

DFT



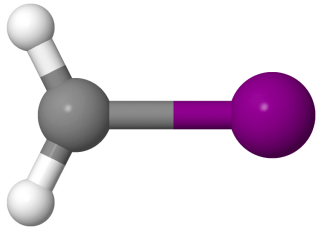
C 0.073540 -1.826604 0.000000

I 0.004053 0.293354 0.000000

H -0.328027 -2.294081 0.976592

H -0.328027 -2.294081 -0.976592

PM7



C 0.229634 -0.001234 0.010442

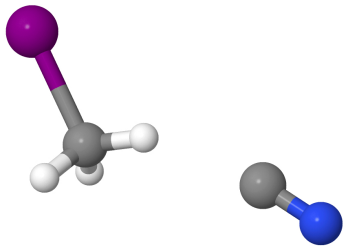
I 2.304750 -0.001234 0.010442

H -0.236930 0.919680 0.010442

H -0.236789 -0.921743 0.012872

16. $\mathbf{NC^-\cdots HCH_2I}$

DFT



C 1.25653 0.42599 -0.00354

H 1.87873 0.44440 0.89503

H 0.50893 1.23671 0.00201

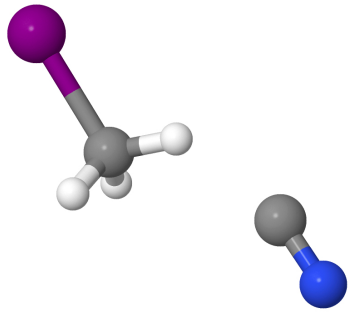
H 1.86633 0.44599 -0.91053

I 0.24883 -1.51354 0.00170

C -0.11349 3.42838 0.00182

N -0.20945 4.60561 0.00102

PM7



C 0.301519 0.400994 0.460560

H 1.390429 0.400994 0.460560

H -0.052667 1.468475 0.460560

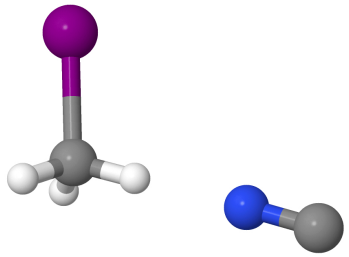
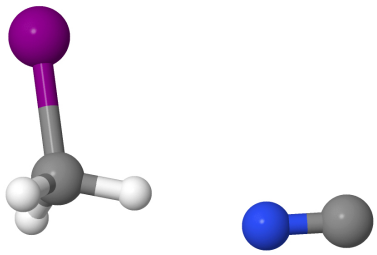
H -0.103144 -0.094383 -0.417761

I -0.357211 -0.646190 2.227900

C 0.326864 3.111556 -0.756451

N 0.769482 3.794943 -1.594395

17. $\mathbf{CN^{-}\cdots HCH_2I}$

DFT	*PM7*
	
C 1.25653 0.42599 -0.00354	C -0.040865 -0.006590 0.023352
H 1.87873 0.44440 0.89503	H 1.043856 -0.006590 0.023352
H 0.50893 1.23671 0.00201	H -0.410490 1.066475 0.023352
H 1.86633 0.44599 -0.91053	H -0.463601 -0.513237 -0.836230
I 0.24883 -1.51354 0.00170	I -0.698834 -0.964851 1.817725
C -0.11349 3.42838 0.00182	N -1.070607 2.920183 -0.098166
N -0.20945 4.60561 0.00102	C -1.633746 3.920138 0.136384