© 1999 American Chemical Society, Macromolecules, Coote ma9818073 Supporting Info Page 1

MA9818073

ARTICLE

Effect of the Penultimate Unit on Radical Stability and Reactivity in Free-Radical Polymerization

Michelle L. Coote and Thomas P. Davis*

School of Chemical Engineering & Industrial Chemistry, The University of New South Wales, Sydney, NSW 2052. Australia

Leo Radom*

Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia

RECEIVED
FEB 4 1999
MACROMOLECULES

Supporting Information

(13 pages)

Gaussian archive entries giving the geometries of all species involved in the calculation of radical stabilities (Table S1), the reaction barriers (Table S3), and the IE and EA values (Table S5). Corresponding total energies required for the calculation of these properties are given in Tables S2, S4 and S6, repectively.

Table S1. Geometries of Species Involved in the Calculation of Gamma Substituent Effects in 1-Y,3-X-Propyl Radicals

propane //B3-LYP/6-31G(d)

```
1\1\GINC-RSCQC8\FOpt\RB3LYP\6-31G(d)\C3H8\MICHELLE\25-Aug-1997\1\\#P B
3LYP/6-31G* OPT=Z-MATRIX FREQ=NORAMAN MAXDISK=1048576000\\Propane C2v\
\0,1\C\X,1,1.\H,1,ch1,2,a1\H,1,ch1,2,a1,3,180.,0\C,1,cc1,2,a2,3,90.,0\
C,1,cc1,2,a2,3,-90.,0\H,5,ch2,1,a3,2,dih2,0\H,5,ch2,1,a3,2,-dih2,0\H,5
,ch3,1,a4,2,0.,0\H,6,ch2,1,a3,2,dih2,0\H,6,ch2,1,a3,2,-dih2,0\H,6,ch3,
1,a4,2,0.,0\\cc1=1.53220705\ch1=1.09852644\ch2=1.09717616\ch3=1.096168
96\a1=53.0238437\a2=123.53345912\a3=111.10713328\a4=111.55790027\dih2=
120.20274075\\Version=IBM-RS6000-G94RevE.1\State=1-A1\HF=-119.1442466\
RMSD=2.430e-09\RMSF=8.521e-06\Dipole=0.,0.,0.0217712\PG=C02V [C2(C1),S
GV(C2H2),SGV'(H2),X(H4)]\\@
```

1F-propane //B3-LYP/6-31G(d)

```
1\1\GINC-RSCQC8\FOpt\RB3LYP\6-31G(d)\C3H7F1\MICHELLE\24-Jul-1997\1\\#P
 B3LYP/6-31G* OPT=Z-MATRIX FREQ MAXDISK=1048576000\\F-Propane C1b\\0,1
\C\C,1,r1\C,2,r2,1,a1\F,1,r3,2,a2,3,dih2,0\H,1,r4,2,a3,3,dih1,0\H,1,r5
,2,a4,3,dih3,0\H,2,r6,1,a5,5,dih4,0\H,2,r7,1,a6,5,dih5,0\H,3,r8,2,a7,1
,dih6,0\H,3,r9,2,a8,1,dih7,0\H,3,r10,2,a9,1,dih8,0\\r1=1.51984515\r2=1
.53129138\r3=1.39577525\r4=1.09733197\r5=1.09842837\r6=1.0975628\r7=1.
09882168\r8=1.09510127\r9=1.09708159\r10=1.09422637\a1=112.84047743\a2
=109.88087046\a3=111.4155308\a4=111.15750183\a5=108.48254657\a6=108.03
```

006322\a7=111.25951265\a8=111.15117585\a9=110.37416276\dih1=179.689480
73\dih2=60.1512406\dih3=-59.0291462\dih4=57.49576615\dih5=-57.79681207
\dih6=182.10072902\dih7=61.88584296\dih8=-57.72290332\\Version=IBM-RS6
000-G94RevE.1\HF=-218.3709804\RMSD=4.152e-09\RMSF=4.415e-05\Dipole=-0.
2883873,0.495267,0.303144\PG=C01 [X(C3H7F1)]\\@

1CN-propane //B3-LYP/6-31G(d)

1\1\GINC-RSCQC8\FOpt\RB3LYP\6-31G(d)\C4H7N1\MICHELLE\25-Jul-1997\1\\#P
B3LYP/6-31G* OPT=Z-MATRIX FREQ MAXDISK=1048576000\\3cn-Propane C1b\\0
,1\C\C,1,r1\C,2,r2,1,a1\C,1,r3,2,a2,3,dih2,0\H,1,r4,2,a3,3,dih1,0\H,1,
r5,2,a4,3,dih3,0\H,2,r6,1,a5,5,dih4,0\H,2,r7,1,a6,5,dih5,0\H,3,r8,2,a7
,1,dih6,0\H,3,r9,2,a8,1,dih7,0\H,3,r10,2,a9,1,dih8,0\X,4,1.,1,90.,2,di
h9,0\N,4,r11,12,a10,2,dih9,0\\r1=1.54512057\r2=1.5303741\r3=1.46715143
\r4=1.09682559\r5=1.09772011\r6=1.09639269\r7=1.09679228\r8=1.09507074
\r9=1.09676353\r10=1.0954821\r11=1.16100242\a1=113.48777361\a2=112.894
93421\a3=110.32016166\a4=110.16032553\a5=108.84024498\a6=107.29571257\
a7=110.70396624\a8=111.21677064\a9=111.24931563\a10=91.03060002\dih1=1
83.51490474\dih2=62.2991933\dih3=-58.81718843\dih4=60.54079644\dih5=-5
4.60543645\dih6=179.4420775\dih7=59.65948124\dih8=-60.60138649\dih9=17
9.76263013\\Version=IBM-RS6000-G94RevE.1\HF=-211.3828777\RMSD=2.532e-0
9\RMSF=1.098e-05\Dipole=-0.6091579,1.2108583,0.7105923\PG=C01 [X(C4H7N
1)]\\@

propyl radical //B3-LYP/6-31G(d)

1\1\GINC-RSCQC8\FOpt\UB3LYP\6-31G(d)\C3H7(2)\MICHELLE\14-Aug-1997\1\\#
N UB3LYP/6-31G* OPT=Z-MATRIX FREQ=NORAMAN MAXDISK=1048576000\\CH3CH2CH
2 gauche-propyl radical (Richrad's)\\0,2\C\C,1,r1\C,1,r2,2,tha1\H,1,r3
,2,tha2,3,dih1,0\H,1,r4,2,tha3,3,-dih2,0\H,2,r5,1,tha4,3,dih3,0\H,2,r6
,1,tha5,3,dih4,0\H,3,r7,1,tha6,2,dih5,0\H,3,r8,1,tha7,8,dih6,0\H,3,r9,
1,tha8,8,-dih7,0\\r1=1.49195439\r2=1.53578685\r3=1.09967767\r4=1.10703
315\r5=1.08669245\r6=1.08571725\r7=1.09577824\r8=1.09679322\r9=1.09572
172\tha1=113.57267451\tha2=109.77177899\tha3=110.01520419\tha4=120.591
09298\tha5=121.12889557\tha6=111.26701277\tha7=110.90921969\tha8=111.0
1470485\dih1=123.33647433\dih2=121.81299739\dih3=32.31654182\dih4=201.
79775409\dih5=181.75363477\dih6=119.94101998\dih7=120.42488896\\Versio
n=IBM-RS6000-G94RevE.1\HF=-118.4713697\S2=0.754\S2-1=0.\S2A=0.75\RMSD=
3.473e-09\RMSF=2.761e-05\Dipole=-0.0353677,0.0400336,-0.0836473\PG=C01
[X(C3H7)]\\@

1F-propyl radical //B3-LYP/6-31G(d)

1\1\GINC-RSCQC8\FOpt\UB3LYP\6-31G(d)\C3H6F1(2)\MICHELLE\14-Aug-1997\1\
\#N UB3LYP/6-31G* OPT=Z-MATRIX FREQ=NORAMAN MAXDISK=1048576000\\CH3CH2
CHF radicali (Richard's)\\0,2\C\C,1,r1\C,1,r2,2,tha1\H,1,r3,2,tha2,3,d
ih1,0\H,1,r4,2,tha3,3,-dih2,0\H,2,r5,1,tha4,3,dih3,0\F,2,r6,1,tha5,3,-
dih4,0\H,3,r7,1,tha6,2,dih5,0\H,3,r8,1,tha7,7,dih6,0\H,3,r9,1,tha8,7,-
dih7,0\\r1=1.48706229\r2=1.54547738\r3=1.09925256\r4=1.09704615\r5=1.0
8886074\r6=1.35700911\r7=1.09583043\r8=1.09459085\r9=1.09573746\tha1=1
13.63177721\tha2=109.03225205\tha3=108.10061764\tha4=123.21987662\tha5
=115.17442563\tha6=110.83791648\tha7=110.30248973\tha8=111.11478797\di
h1=121.70219808\dih2=122.49551543\dih3=80.09924937\dih4=63.86457222\di
h5=177.73364974\dih6=30.1961346\dih7=89.57669006\\Version=IBM-RS6000-G
94RevE.1\HF=-217.7049504\S2=0.753\S2-1=0.\S2A=0.75\RMSD=3.660e-09\RMSF
=8.990e-06\Dipole=-0.0218873,0.415763,-0.3750585\PG=C01 [X(C3H6F1)]\\@

1F,3F-propyl radical //B3-LYP/6-31G(d)

1\1\GINC-PC\FOpt\UB3LYP\6-31G(d)\C3H5F2(2)\MLC501\18-May-1998\1\\#N B3
LYP/6-31G* OPT=Z-MATRIX FREQ=NORAMAN MAXDISK=5242880000\\1f 3f-propyl
radical opp\\0,2\C\C,1,r1\C,1,r2,2,tha1\H,1,r3,2,tha2,3,dih1,0\H,1,r4,
2,tha3,3,-dih2,0\F,2,r5,1,tha4,3,dih3,0\H,2,r6,1,tha5,3,-dih4,0\H,3,r7
,1,tha6,2,dih5,0\F,3,r8,1,tha7,7,dih6,0\H,3,r9,1,tha8,7,-dih7,0\\r1=1.
48688899\r2=1.53311558\r5=1.35590922\r4=1.09997052\r3=1.09608591\r6=1.
08691408\r7=1.09708373\r8=1.39099079\r9=1.09594283\tha1=113.38270771\t

ha2=108.94715441\tha3=109.86330308\tha4=114.63782889\tha5=123.07833904
\tha6=110.91138661\tha7=109.47538707\tha8=110.43387328\dih1=121.652146
78\dih2=120.78936476\dih3=63.9008187\dih4=79.71233399\dih5=181.6452501
7\dih6=37.63921676\dih7=81.58254194\\Version=SGI-G94RevE.2\HF=-316.930
5653\S2=0.753\S2-1=0.\S2A=0.75\RMSD=5.366e-09\RMSF=3.536e-05\Dipole=-0
.3846061,0.0892039,-0.4734785\PG=C01 [X(C3H5F2)]\\@

1F,3CN-propyl radical //B3-LYP/6-31G(d)

1\1\GINC-RSCQC8\FOpt\UB3LYP\6-31G(d)\C4H5F1N1(2)\MICHELLE\15-Aug-1997\
1\\#N UB3LYP/6-31G* OPT=Z-MATRIX FREQ=NORAMAN MAXDISK=1048576000\\NCCH
2CH2CHF radical (Richard's)\\0,2\C\C,1,r1\C,1,r2,2,tha1\H,1,r3,2,tha2,
3,dih1,0\H,1,r4,2,tha3,3,-dih2,0\H,2,r5,1,tha4,3,dih3,0\F,2,r6,1,tha5,
3,-dih4,0\C,3,r7,1,tha6,2,dih5,0\H,3,r8,1,tha7,8,dih6,0\H,3,r9,1,tha8,
8,-dih7,0\X,8,1.,3,90.,1,180.,0\N,8,r10,11,tha9,3,dih8,0\\r1=1.4846998
2\r2=1.55985974\r3=1.0979415\r4=1.09491115\r5=1.08667706\r6=1.35369668
\r7=1.46484847\r8=1.09573479\r9=1.0965362\r10=1.16086515\tha1=113.7024
7234\tha2=109.58687181\tha3=109.09651192\tha4=123.93343294\tha5=114.71
352277\tha6=112.59398871\tha7=109.09146788\tha8=109.96734034\tha9=91.4
22539\dih1=119.65126784\dih2=122.76292761\dih3=82.84820533\dih4=63.195
70897\dih5=-66.02821118\dih6=121.0791339\dih7=121.43226633\dih8=180.27
396468\\Version=IBM-RS6000-G94RevE.1\HF=-309.9422119\S2=0.753\S2-1=0.\
S2A=0.75\RMSD=3.773e-09\RMSF=2.871e-05\Dipole=-0.8644157,-0.8346352,-0
.5256826\PG=C01 [X(C4H5F1N1)]\\@

1CN-propyl radical //B3-LYP/6-31G(d)

1\1\GINC-RSCQC2\FOpt\UB3LYP\6-31G(d)\C4H6N1(2)\MICHELLE\20-Jun-1998\1\
\#N UB3LYP/6-31G* OPT=Z-MATRIX FREQ=NORAMAN MAXDISK=786432000\\1CN-pro
pyl (Rich) Rad\\0,2\C\C,1,r1\C,1,r2,2,tha1\H,1,r3,2,tha2,3,dih1,0\H,1,
r4,2,tha3,3,-dih2,0\H,2,r5,1,tha4,3,dih3,0\C,2,r6,1,tha5,3,-dih4,0\X,7
,1.,2,90.,1,0.,0\N,7,r7,8,tha6,2,dih5,0\H,3,r8,1,tha7,2,dih6,0\H,3,r9,
1,tha8,10,dih7,0\H,3,r10,1,tha9,10,-dih8,0\\r1=1.50077117\r2=1.5403703
2\r3=1.09474656\r4=1.10146853\r5=1.08779019\r6=1.38701577\r7=1.1768914
1\r8=1.09515644\r9=1.09595542\r10=1.09475926\tha1=112.56314173\tha2=10
9.84849418\tha3=108.57273937\tha4=119.05269054\tha5=123.43561478\tha6=
89.4792779\tha7=110.32729552\tha8=111.17416667\tha9=111.06136049\dih1=
123.36820065\dih2=120.38431406\dih3=55.00054633\dih4=124.73660834\dih5
=180.04263995\dih6=182.57751884\dih7=119.70626148\dih8=120.03343206\\V
ersion=IBM-RS6000-G94RevE.1\HF=-210.730079\S2=0.767\S2-1=0.\S2A=0.75\R
MSD=4.692e-09\RMSF=9.438e-06\Dipole=0.7209754,0.9724939,-1.0021008\PG=
C01 [X(C4H6N1)]\\@

1CN,3F-propyl radical //B3-LYP/6-31G(d)

1\1\GINC-RSCQC2\FOpt\UB3LYP\6-31G(d)\C4H5F1N1(2)\MICHELLE\21-Jun-1998\
1\\#N UB3LYP/6-31G* OPT=Z-MATRIX FREQ=NORAMAN MAXDISK=786432000\\3CN-1
F-propyl Rad3\\0,2\C\C,1,r1\C,1,r2,2,tha1\H,1,r3,2,tha2,3,dih1,0\H,1,r
4,2,tha3,3,-dih2,0\H,2,r5,1,tha4,3,dih3,0\C,2,r6,1,tha5,3,-dih4,0\X,7,
1.,2,90.,1,0.,0\N,7,r7,8,tha6,2,dih5,0\H,3,r8,1,tha7,2,dih6,0\F,3,r9,1
,tha8,10,dih7,0\H,3,r10,1,tha9,10,-dih8,0\\r1=1.49984363\r2=1.52747766
\r3=1.09564786\r4=1.10162063\r5=1.08590365\r6=1.38620943\r7=1.17668504
\r8=1.09623622\r9=1.39234756\r10=1.09600732\tha1=111.93392169\tha2=111
.04144563\tha3=109.25086993\tha4=118.45854437\tha5=123.0274991\tha6=89
.41010799\tha7=110.67591961\tha8=109.03787876\tha9=111.32504634\dih1=1
22.91175079\dih2=119.33602681\dih3=43.3517504\dih4=138.51766821\dih5=1
80.32717743\dih6=183.57403227\dih7=119.13413788\dih8=121.5905284\\Vers
ion=IBM-RS6000-G94RevE.1\HF=-309.9557143\S2=0.767\S2-1=0.\S2A=0.75\RMS
D=9.662e-09\RMSF=1.856e-05\Dipole=0.5500866,0.3058817,-1.1559154\PG=C0
1 [X(C4H5F1N1)]\\@

1CN,3CN-propyl radical //B3-LYP/6-31G(d)

1\1\GINC-RSCQC2\FOpt\UB3LYP\6-31G(d)\C5H5N2(2)\MICHELLE\21-Jun-1998\1\
\#N UB3LYP/6-31G* OPT=Z-MATRIX FREQ=NORAMAN MAXDISK=786432000\\3CN,1CN
-propyl (Rich) Rad3\\0,2\C\C,1,r1\C,1,r2,2,tha1\H,1,r3,2,tha2,3,dih1,0
\H,1,r4,2,tha3,3,-dih2,0\H,2,r5,1,tha4,3,dih3,0\C,2,r6,1,tha5,3,dih4,0

\X,7,1.,2,90.,1,0.,0\N,7,r7,8,tha6,2,dih5,0\C,3,r8,1,tha7,2,dih6,0\H,3
,r9,1,tha8,10,dih7,0\H,3,r10,1,tha9,10,-dih8,0\X,10,1.,3,90.,1,180.,0\
N,10,r11,13,tha10,3,dih9,0\\r1=1.50040229\r2=1.55314239\r3=1.09363006\
r4=1.0994371\r5=1.08715109\r6=1.38625861\r7=1.17668105\r8=1.46571558\r
9=1.09597018\r10=1.09634253\r11=1.16074559\tha1=113.00399606\tha2=110.
45104629\tha3=109.31967058\tha4=119.16535427\tha5=122.60294303\tha6=89
.30377851\tha7=112.46873233\tha8=110.12725887\tha9=109.3540274\tha10=9
1.73111178\dih1=121.53245355\dih2=120.59728543\dih3=57.02873402\dih4=2
36.78992479\dih5=180.05387457\dih6=-59.97573489\dih7=121.50801197\dih8
=120.8777105\dih9=179.83599869\\Version=IBM-RS6000-G94RevE.1\HF=-302.9
651618\S2=0.767\S2-1=0.\S2A=0.75\RMSD=6.690e-09\RMSF=2.837e-05\Dipole=
-0.1653959,-0.1949689,-1.2575902\PG=C01 [X(C5H5N2)]\\@

Table S2. Total Energies (Hartrees) Required for the Calculation of Gamma Substituent Effects in 1-Y,3-X-Propyl Radicals

Species	Energy[a]	ZPVE[b]	Energy[c]
1X-propanes:			
propane	-118.83878	0.10410	-118.73669
1F-propane	-217.96786	0.09735	-217.87240
1CN-propane	-210.92345	0.10356	-210.82189
propyl radical:	-118.16944	0.08874	-118.08243
1F,3X-propyl radicals:			
1F-propyl	-217.30176	0.08313	-217.22024
1F,3F-propyl	-316.42979	0.07629	-316.35498
1F,3CN-propyl	-309.38449	0.08236	-309.30373
1CN,3X-propyl radicals:			
1CN-propyl	-210.26735	0.08942	-210.17967
1CN,3F-propyl	-309.39459	0.08253	-309.31367
1CN,3CN-propyl	-302.34834	0.08870	-302.26136

[a] RMP2/6-311+G(3df,2p)//B3-LYP/6-31G(d) [b] Calculated using B3-LYP/6-31G(d) frequencies. [c] Including ZPVE, scaled by 0.9806.

Table S3. Geometries of Species Involved in the Calculation of Reaction Barriers

CH_2CH_2 //HF/6-31G(d)

1\1\ UNSW-SKYWALKER\FOpt\UHF\6-31G(d)\C2H4\MICHELLE\28-Aug-1996\1\\#P
UHF/6-31G* FOPT=Z-MATRIX GEOM=CHECK GUESS=READ\\C2H4 D2h\\0,1\C\C,1,R2
1\H,1,R31,2,A312\H,2,R31,1,A312,3,0.,0\H,2,R31,1,A312,3,180.,0\H,1,R31
,2,A312,4,180.,0\\R21=1.31700415\R31=1.07600669\A312=121.80462264\\Ver
sion=SGI-G94RevB.1\State=1-AG\HF=-78.0317181\S2=0.\S2-1=0.\S2A=0.\RMSD
=1.764e-09\RMSF=3.999e-05\Dipole=0.,0.,0.\PG=D02H [C2"(C1.C1),SG(H4)]\
\@

1F-propyl radical //HF/6-31G(d) [from Ref 27]

1\1\episarch-Convex/C-1/SN8484\FOPT\UHF\6-31G(D)\C3H6F1(2)\9-Dec-1992\
1\\#N UHF 6-31G* OPT=READFC SCFCYC=150 SCF=INCORE GUESS=READ\\CH3CH2CH
F radical 6-31g* opt\\0,2\C\C,1,r1\C,1,r2,2,tha1\H,1,r3,2,tha2,3,dih1,
0\H,1,r4,2,tha3,3,-dih2,0\H,2,r5,1,tha4,3,dih3,0\F,2,r6,1,tha5,3,-dih4
,0\H,3,r7,1,tha6,2,dih5,0\H,3,r8,1,tha7,7,dih6,0\H,3,r9,1,tha8,7,-dih7
,0\\r1=1.492381\r2=1.535779\r3=1.086403\r4=1.085861\r5=1.076328\r6=1.3
42205\r7=1.085037\r8=1.083891\r9=1.085673\tha1=113.068048\tha2=108.693
479\tha3=108.191314\tha4=121.669560\tha5=114.314381\tha6=110.721656\th
a7=110.627251\tha8=111.131778\dih1=121.820100\dih2=122.210845\dih3=75.
320664\dih4=63.880454\dih5=178.761115\dih6=31.160601\dih7=88.893880\\V
ersion=CONVEX-UNIX-G90RevJ\HF=-216.4827997\S2=0.759\S2-1=0.000\S2A=0.7
50\RMSD=0.176E-08\RMSF=0.551E-04\Dipole=-0.0753090,0.5264518,-0.419251
4\PG=C01 [X(C3H6F1)]\\@

1F,3F-propyl radical //HF/6-31G(d)

1\1\GINC-RSCQC8\FOpt\UHF\6-31G(d)\C3H5F2(2)\MICHELLE\14-May-1998\1\\#N
UHF/6-31G* OPT=Z-MATRIX FREQ=NORAMAN MAXDISK=1048576000\\1f,3f-propyl
radical opp\\0,2\C\C,1,r1\C,1,r2,2,tha1\H,1,r3,2,tha2,3,dih1,0\H,1,r4
,2,tha3,3,-dih2,0\F,2,r5,1,tha4,3,dih3,0\H,2,r6,1,tha5,3,-dih4,0\H,3,r
7,1,tha6,2,dih5,0\F,3,r8,1,tha7,7,dih6,0\H,3,r9,1,tha8,7,-dih7,0\\r1=1
.49245529\r2=1.52156423\r5=1.34141207\r4=1.08690221\r3=1.0847565\r6=1.
0741441\r7=1.0822648\r8=1.37202619\r9=1.08112523\tha1=112.79491993\tha
2=108.9451029\tha3=109.37116648\tha4=113.74984852\tha5=121.66672069\th
a6=111.13523647\tha7=109.23415726\tha8=111.17292548\dih1=121.46368047\
dih2=120.92781013\dih3=64.08933435\dih4=75.12923994\dih5=180.29408855\
dih6=37.32672007\dih7=81.68554762\\Version=IBM-RS6000-G94RevE.1\HF=-31
5.3310437\S2=0.759\S2-1=0.\S2A=0.75\RMSD=6.970e-09\RMSF=1.513e-05\Dipo
le=-0.4791561,0.0606541,-0.5680176\PG=C01 [X(C3H5F2)]\\@

1F,3CN-propyl radical //HF/6-31G(d) [from Ref 22]

1\1\ ANU-VP\FOPT\UHF\6-31G(D)\C4H5F1N1(2)\MWW501\11-Apr-1993\1\\#N UHF
6-31G* OPT=READFC GUESS=READ GEOM=CHECK SCFCYC=150 SCF=(QC,DIRECT)\\N
CCH2CH2CHF radical 6-31g* opt\\0,2\C\C,1,r1\C,1,r2,2,tha1\H,1,r3,2,tha
2,3,dih1,0\H,1,r4,2,tha3,3,-dih2,0\H,2,r5,1,tha4,3,dih3,0\F,2,r6,1,tha
5,3,-dih4,0\C,3,r7,1,tha6,2,dih5,0\H,3,r8,1,tha7,8,dih6,0\H,3,r9,1,tha
8,8,-dih7,0\X,8,1.,3,90.,1,180.,0\N,8,r10,11,tha9,3,dih8,0\\r1=1.49176
162\r2=1.5431801\r3=1.08518577\r4=1.08379155\r5=1.07446493\r6=1.339616
4\r7=1.47279944\r8=1.08280239\r9=1.08352914\r10=1.1351372\tha1=113.342
00483\tha2=108.94717287\tha3=109.10059198\tha4=122.2545085\tha5=113.64
420702\tha6=112.27165402\tha7=110.06979597\tha8=110.18089249\tha9=91.1
128899\dih1=119.86585143\dih2=122.82676542\dih3=77.57146225\dih4=62.72
217948\dih5=-65.61459459\dih6=120.87040957\dih7=120.48834211\dih8=180.
20842842\\Version=Fujitsu-VP-Unix-G92RevC.3\HF=-308.2152929\S2=0.759\S
2-1=0.\S2A=0.75\RMSD=0.000e+00\RMSF=1.820e-05\Dipole=-0.9500966,-0.799
4034,-0.6294369\PG=C01 [X(C4H5F1N1)]\\@

1F-propyl+CH_2CH_2 Transition Structure //HF/6-31G(d)

1\1\GINC-RSCQC9\FTS\UHF\6-31G(d)\C5H10F1(2)\MICHELLE\11-Jun-1994\1\\#N
UHF/6-31G(D) OPT=(TS,Z-MATRIX,CALCFC) FREQ=NORAMAN SCF=(QC,DIRECT) MA
XDISK=1048576000\\radical(1X=F) + monomer(X=H) TS: C1 symmetry\\0,2\C\

C,1,cca\C,2,ccb,1,a1\C,3,ccc,2,a2,1,dih1,0\C,4,ccd,3,a3,2,dih2,0\H,1,c
ha,2,a4,3,dih3,0\H,1,chb,2,a5,3,dih4,0\H,1,chc,2,a6,3,dih5,0\H,2,chd,1
,a7,3,dih6,0\H,2,che,1,a8,3,dih7,0\H,3,chf,2,a9,4,dih8,0\F,3,chg,2,a10
,4,dih9,0\H,4,chh,5,a11,3,dih10,0\H,4,cfi,5,a12,3,dih11,0\H,5,chj,4,a1
3,3,dih12,0\H,5,chm,4,a14,3,dih13,0\\cca=1.5339826\ccb=1.49919819\ccc=
2.23139122\ccd=1.38149839\cha=1.08522735\chb=1.08592544\chc=1.08372189
\chd=1.0863946\che=1.0862986\chf=1.07747256\chg=1.35133683\chh=1.07629
54\cfi=1.07545379\chj=1.07469467\chm=1.07543932\a1=112.89808292\a2=108
.33533439\a3=108.48578112\a4=110.75390387\a5=111.14448464\a6=110.69603
705\a7=109.50400369\a8=109.99771119\a9=117.84494718\a10=112.40697365\a
11=119.74312849\a12=119.49703506\a13=121.18607945\a14=121.38337578\dih
1=175.45924396\dih2=175.594641\dih3=180.79457118\dih4=60.85112859\dih5
=-59.20561758\dih6=121.56432168\dih7=-121.0270342\dih8=116.65291766\di
h9=-113.32747894\dih10=106.10495314\dih11=-100.257276\dih12=83.1486599
9\dih13=-89.8866278\\Version=IBM-RS6000-G94RevE.1\HF=-294.5000991\S2=1
.028\S2-1=0.\S2A=0.76\RMSD=0.000e+00\RMSF=2.317e-06\Dipole=-0.416629,-
0.4965485,-0.0061417\PG=C01 [X(C5H10F1)]\\@

1F,3F-propyl+CH_2CH_2 Transition Structure //HF/6-31G(d)

1\1\GINC-RSCQC9\FTS\UHF\6-31G(d)\C5H9F2(2)\MICHELLE\10-Jun-1994\1\\#N
UHF/6-31G(D) OPT=(TS,Z-MATRIX,CALCFC) FREQ=NORAMAN SCF=(QC,DIRECT) MAX
DISK=1048576000\\radical(1X=F 3X=F) + monomer(X=H) TS: C1 symmetry\\0,
2\C\C,1,cca\C,2,ccb,1,a1\C,3,ccc,2,a2,1,dih1,0\C,4,ccd,3,a3,2,dih2,0\F
,1,cfa,2,a4,3,dih3,0\H,1,chb,2,a5,3,dih4,0\H,1,chc,2,a6,3,dih5,0\H,2,c
hd,1,a7,3,dih6,0\H,2,che,1,a8,3,dih7,0\H,3,chf,2,a9,4,dih8,0\F,3,chg,2
,a10,4,dih9,0\H,4,chh,5,a11,3,dih10,0\H,4,cfi,5,a12,3,dih11,0\H,5,chj,
4,a13,3,dih12,0\H,5,chm,4,a14,3,dih13,0\\cca=1.52017451\ccb=1.49931666
\ccc=2.23559664\ccd=1.38108442\cfa=1.37287941\chb=1.08246338\chc=1.080
92538\chd=1.0867976\che=1.08515954\chf=1.07498388\chg=1.35121824\chh=1
.07631097\cfi=1.07562247\chj=1.07460954\chm=1.07529048\a1=112.70937441
\a2=108.19216955\a3=108.03318018\a4=109.27583187\a5=111.16766297\a6=11
1.23244084\a7=108.50662053\a8=109.08057779\a9=117.80497713\a10=111.856
63491\a11=119.76899414\a12=119.49224065\a13=121.19025987\a14=121.36110
55\dih1=176.14350577\dih2=177.80259229\dih3=61.62908093\dih4=180.54120
869\dih5=-57.41239702\dih6=121.55289946\dih7=-121.28809529\dih8=116.75
800794\dih9=-113.26041572\dih10=105.74771319\dih11=-100.41510134\dih12
=83.47490577\dih13=-89.67098055\\Version=IBM-RS6000-G94RevE.1\HF=-393.
348593\S2=1.029\S2-1=0.\S2A=0.76\RMSD=0.000e+00\RMSF=2.036e-05\Dipole=
-0.6868601,0.081074,0.3394429\PG=C01 [X(C5H9F2)]\\@

1F,3CN-propyl+CH_2CH_2 Transition Structure //HF/6-31G(d)

1\1\GINC-RSCQC9\FTS\UHF\6-31G(d)\C6H9F1N1(2)\MICHELLE\11-Jun-1994\1\\#
N UHF/6-31G(D) OPT=(TS,Z-MATRIX,CALCFC) FREQ=NORAMAN SCF=(QC,DIRECT) M
AXDISK=1048576000\\radical(1X=F 3X=CN) + monomer(X=H) TS: C1 symmetry\
\0,2\C\C,1,cca\C,2,ccb,1,a1\C,3,ccc,2,a2,1,dih1,0\C,4,ccd,3,a3,2,dih2,
0\C,1,cha,2,a4,3,dih3,0\H,1,chb,2,a5,3,dih4,0\H,1,chc,2,a6,3,dih5,0\H,
2,chd,1,a7,3,dih6,0\H,2,che,1,a8,3,dih7,0\H,3,chf,2,a9,4,dih8,0\F,3,ch
g,2,a10,4,dih9,0\H,4,chh,5,a11,3,dih10,0\H,4,cfi,5,a12,3,dih11,0\H,5,c
hj,4,a13,3,dih12,0\H,5,chm,4,a14,3,dih13,0\X,6,1.,1,90.,2,180.,0\N,6,c
na,17,a18,1,dih17,0\\cca=1.54165818\ccb=1.49911114\ccc=2.23625206\ccd=
1.38125621\cha=1.47308241\chb=1.08373241\chc=1.08264314\chd=1.08501509
\che=1.08417375\chf=1.07579451\chg=1.35039209\chh=1.07636001\cfi=1.075
69318\chj=1.07452812\chm=1.07515895\a1=113.18798191\a2=107.96229544\a3
=107.69338594\a4=112.31110381\a5=110.24610487\a6=110.07800226\a7=107.6
2534022\a8=109.80947412\a9=118.22525394\a10=111.6570732\a11=119.740725
16\a12=119.46161357\a13=121.18236875\a14=121.35109815\dih1=174.4355562
9\dih2=178.36683994\dih3=66.14401974\dih4=186.55200427\dih5=-54.744123
24\dih6=120.71037286\dih7=-122.36108807\dih8=116.54108532\dih9=-113.19
590389\dih10=105.71851211\dih11=-100.4998552\dih12=83.63366776\dih13=-
89.6961511\cna=1.13521786\a18=91.08759917\dih17=179.73983148\\Version=
IBM-RS6000-G94RevE.1\HF=-386.2330604\S2=1.029\S2-1=0.\S2A=0.76\RMSD=0.
000e+00\RMSF=1.929e-05\Dipole=-0.9079087,0.8319213,0.7951172\PG=C01 [X
(C6H9F1N1)]\\@

1CN-propyl radical //HF/6-31G(d) [recalculated, geometry from Ref 27]

1\1\GINC-RSCQC2\FOpt\UHF\6-31G(d)\C4H6N1(2)\MICHELLE\22-Jun-1998\1\\#N
UHF/6-31G* OPT=(MAXCYCLE=1000,Z-MATRIX) FREQ=NORAMAN MAXDISK=786432000\\1CN-propyl (Rich) Rad\\0,2\C\C,1,r1\C,1,r2,2,tha1\H,1,r3,2,tha2,3,dih1,0\H,1,r4,2,tha3,3,-dih2,0\H,2,r5,1,tha4,3,dih3,0\C,2,r6,1,tha5,3,-dih4,0\X,7,1.,2,90.,1,0.,0\N,7,r7,8,tha6,2,dih5,0\H,3,r8,1,tha7,2,dih6,0\H,3,r9,1,tha8,10,dih7,0\H,3,r10,1,tha9,10,-dih8,0\\r1=1.50612564\r2=1.53192597\r3=1.08369663\r4=1.08801222\r5=1.0752302\r6=1.39360787\r7=1.15906707\r8=1.08459014\r9=1.08562807\r10=1.08465422\tha1=112.24927149\tha2=109.56269407\tha3=108.63624937\tha4=119.80671745\tha5=122.99454791\tha6=89.59494636\tha7=110.44280935\tha8=111.15388962\tha9=111.11418737\dih1=122.73866581\dih2=120.97782492\dih3=53.03914003\dih4=128.19965426\dih5=180.24646028\dih6=181.70798978\dih7=119.67178031\dih8=120.00905216\\Version=IBM-RS6000-G94RevE.1\HF=-209.3817462\S2=0.917\S2-1=0.\S2A=0.767\RMSD=7.544e-09\RMSF=1.021e-05\Dipole=0.7855753,0.9640065,-0.9749837\PG=C01 [X(C4H6N1)]\\@

1CN,3F-propyl radical //HF/6-31G(d)

1\1\GINC-RSCQC2\FOpt\UHF\6-31G(d)\C4H5F1N1(2)\MICHELLE\20-Jun-1998\1\\#N UHF/6-31G* OPT=Z-MATRIX FREQ=NORAMAN MAXDISK=786432000\\3CN-1F-propyl Rad3\\0,2\C\C,1,r1\C,1,r2,2,tha1\H,1,r3,2,tha2,3,dih1,0\H,1,r4,2,tha3,3,-dih2,0\H,2,r5,1,tha4,3,dih3,0\C,2,r6,1,tha5,3,-dih4,0\X,7,1.,2,90.,1,0.,0\N,7,r7,8,tha6,2,dih5,0\H,3,r8,1,tha7,2,dih6,0\F,3,r9,1,tha8,10,dih7,0\H,3,r10,1,tha9,10,-dih8,0\\r1=1.50504491\r2=1.51826236\r3=1.08439624\r4=1.0875224\r5=1.07348928\r6=1.39320946\r7=1.15895593\r8=1.08186692\r9=1.37160193\r10=1.08187115\tha1=111.87261557\tha2=110.51190392\tha3=109.23609605\tha4=119.54597844\tha5=122.41887295\tha6=89.43552228\tha7=110.93877908\tha8=109.04952962\tha9=111.62788397\dih1=122.05978622\dih2=120.05829957\dih3=46.13803806\dih4=136.96223951\dih5=180.49896934\dih6=182.63747637\dih7=118.82728633\dih8=122.11813748\\Version=IBM-RS6000-G94RevE.1\HF=-308.2296754\S2=0.918\S2-1=0.\S2A=0.767\RMSD=8.802e-09\RMSF=1.247e-05\Dipole=0.5088016,0.2700801,-1.1520898\PG=C01 [X(C4H5F1N1)]\\@

1CN,3CN-propyl radical //HF/6-31G(d) [recalculated, geometry from Ref 22]

1\1\GINC-RSCQC2\FOpt\UHF\6-31G(d)\C5H5N2(2)\MICHELLE\20-Jun-1998\1\\#N
UHF/6-31G* OPT=Z-MATRIX FREQ=NORAMAN MAXDISK=786432000\\3CN,1CN-propyl (Rich) Rad3\\0,2\C\C,1,r1\C,1,r2,2,tha1\H,1,r3,2,tha2,3,dih1,0\H,1,r4,2,tha3,3,-dih2,0\H,2,r5,1,tha4,3,dih3,0\C,2,r6,1,tha5,3,dih4,0\X,7,1.,2,90.,1,0.,0\N,7,r7,8,tha6,2,dih5,0\C,3,r8,1,tha7,2,dih6,0\H,3,r9,1,tha8,10,dih7,0\H,3,r10,1,tha9,10,-dih8,0\X,10,1.,3,90.,1,180.,0\N,10,r11,13,tha10,3,dih9,0\\r1=1.50558043\r2=1.54047006\r3=1.08259234\r4=1.08557524\r5=1.07452146\r6=1.39274898\r7=1.15932977\r8=1.47276668\r9=1.08339675\r10=1.08354814\r11=1.13497943\tha1=112.93758593\tha2=109.98346224\tha3=109.22664007\tha4=120.01639109\tha5=122.11897586\tha6=89.25754136\tha7=112.19081277\tha8=110.6616731\tha9=109.7638039\tha10=91.35256827\dih1=120.96366535\dih2=121.3914599\dih3=62.57412195\dih4=242.85380156\dih5=180.05399772\dih6=-61.64898058\dih7=121.12059516\dih8=120.20976913\dih9=179.8704261\\Version=IBM-RS6000-G94RevE.1\HF=-301.1122901\S2=0.922\S2-1=0.\S2A=0.768\RMSD=7.711e-09\RMSF=2.713e-06\Dipole=-0.2903182,-0.2007471,-1.2409574\PG=C01 [X(C5H5N2)]\\@

1CN-propyl+CH_2CH_2 Transition Structure //HF/6-31G(d)

1\1\GINC-RSCQC8\FTS\UHF\6-31G(d)\C6H10N1(2)\MICHELLE\23-Jun-1998\1\\#N
UHF/6-31G* OPT=(TS,CALCFC,Z-MATRIX) FREQ=NORAMAN MAXDISK=1048576000\\radical(1X=CN) + monomer(X=H) TS: C1 symmetry\\0,2\C\C,1,cca\C,2,ccb,1,a1\C,3,ccc,2,a2,1,dih1,0\C,4,ccd,3,a3,2,dih2,0\H,1,cha,2,a4,3,dih3,0\H,1,chb,2,a5,3,dih4,0\H,1,chc,2,a6,3,dih5,0\H,2,chd,1,a7,3,dih6,0\H,2,che,1,a8,3,dih7,0\H,3,chf,2,a9,4,dih8,0\C,3,chg,2,a10,4,dih9,0\H,4,chh,5,a11,3,dih10,0\H,4,cfi,5,a12,3,dih11,0\H,5,chj,4,a13,3,dih12,0\H,5,chm,4,a14,3,dih13,0\X,12,1.,3,90.,2,180.,0\N,12,cnb,17,a19,3,dih18,0\\cca=1.53303062\ccb=1.51695824\ccc=2.16577362\ccd=1.39240142\cha=1.08517793\chb=1.08557972\chc=1.0845419\chd=1.08512869\che=1.08515075\chf=1.07647809\chg=1.43403008\chh=1.0760305\cfi=1.07565846\chj=1.07437262\chm

=1.07513791\a1=112.98253229\a2=104.68289448\a3=109.77002553\a4=110.398
85452\a5=111.13258838\a6=111.22594571\a7=109.60927226\a8=109.40273492\
a9=116.09660312\a10=117.0131637\a11=118.80482047\a12=118.85829686\a13=
121.14839382\a14=121.16027616\dih1=184.73478169\dih2=175.87767816\dih3
=178.90974657\dih4=59.2062339\dih5=-61.19798711\dih6=122.25825787\dih7
=-120.76358147\dih8=107.660615\dih9=-114.63922509\dih10=105.24911836\d
ih11=-105.90013895\dih12=85.67013143\dih13=-86.45432233\cnb=1.14375466
\a19=90.1074633\dih18=177.88687299\\Version=IBM-RS6000-G94RevE.1\HF=-2
87.3909407\S2=1.082\S2-1=0.\S2A=0.804\RMSD=5.170e-09\RMSF=2.170e-05\Di
pole=-0.9159612,-1.317845,0.1874554\PG=C01 [X(C6H10N1)]\\@

1CN,3F-propyl+CH_2CH_2 Transition Structure //HF/6-31G(d)

1\1\GINC-RSCQC8\FTS\UHF\6-31G(d)\C6H9F1N1(2)\MICHELLE\23-Jun-1998\1\\#
N UHF/6-31G* OPT=(TS,CALCFC,Z-MATRIX) FREQ=NORAMAN MAXDISK=1048576000\
\radical(1X=CN 3X=F) + monomer(X=H) TS: C1 symmetry\\0,2\C\C,1,cca\C,2
,ccb,1,a1\C,3,ccc,2,a2,1,dih1,0\C,4,ccd,3,a3,2,dih2,0\F,1,cfa,2,a4,3,d
ih3,0\H,1,chb,2,a5,3,dih4,0\H,1,chc,2,a6,3,dih5,0\H,2,chd,1,a7,3,dih6,
0\H,2,che,1,a8,3,dih7,0\H,3,chf,2,a9,4,dih8,0\C,3,chg,2,a10,4,dih9,0\H
,4,chh,5,a11,3,dih10,0\H,4,cfi,5,a12,3,dih11,0\H,5,chj,4,a13,3,dih12,0
\H,5,chm,4,a14,3,dih13,0\X,12,1.,3,90.,2,180.,0\N,12,cnb,17,a19,3,dih1
8,0\\cca=1.51992637\ccb=1.51589664\ccc=2.16995475\ccd=1.39184031\cfa=1
.37147598\chb=1.08240529\chc=1.08184415\chd=1.08545466\che=1.08432989\
chf=1.07470618\chg=1.43336886\chh=1.07599874\cfi=1.07582057\chj=1.0743
2941\chm=1.07499348\a1=112.69615436\a2=104.53391006\a3=109.51627739\a4
=109.10160329\a5=110.82494198\a6=111.77833244\a7=108.7400758\a8=108.32
974535\a9=115.73159528\a10=116.68062348\a11=118.81332052\a12=118.87503
788\a13=121.15731791\a14=121.13358533\dih1=188.82979652\dih2=177.39574
681\dih3=60.43720287\dih4=179.14252099\dih5=-58.85105937\dih6=122.5578
8223\dih7=-120.76052458\dih8=107.57906336\dih9=-114.70123211\dih10=104
.95062453\dih11=-105.9353527\dih12=85.9362707\dih13=-86.32712065\cnb=1
.14378824\a19=90.54394377\dih18=177.82529952\\Version=IBM-RS6000-G94Re
vE.1\HF=-386.2388137\S2=1.084\S2-1=0.\S2A=0.805\RMSD=3.601e-09\RMSF=5.
589e-05\Dipole=-1.1498531,-0.7824177,0.4538302\PG=C01 [X(C6H9F1N1)]\\@

1CN,3CN-propyl+CH_2CH_2 Transition Structure //HF/6-31G(d)

1\1\GINC-RSCQC8\FTS\UHF\6-31G(d)\C7H9N2(2)\MICHELLE\23-Jun-1998\1\\#N
UHF/6-31G* OPT=(TS,CALCFC,Z-MATRIX) FREQ MAXDISK=1048576000\\radical(1
X=CN 3X=CN) + monomer(X=H) TS: C1 symmetry\\0,2\C\C,1,cca\C,2,ccb,1,a1
\C,3,ccc,2,a2,1,dih1,0\C,4,ccd,3,a3,2,dih2,0\C,1,cha,2,a4,3,dih3,0\H,1
,chb,2,a5,3,dih4,0\H,1,chc,2,a6,3,dih5,0\H,2,chd,1,a7,3,dih6,0\H,2,che
,1,a8,3,dih7,0\H,3,chf,2,a9,4,dih8,0\C,3,chg,2,a10,4,dih9,0\H,4,chh,5,
a11,3,dih10,0\H,4,cfi,5,a12,3,dih11,0\H,5,chj,4,a13,3,dih12,0\H,5,chm,
4,a14,3,dih13,0\X,6,1.,1,90.,2,180.,0\N,6,cna,17,a18,1,dih17,0\X,12,1.
,3,90.,2,180.,0\N,12,cnb,19,a19,3,dih18,0\\cca=1.54098857\ccb=1.515771
31\ccc=2.17268394\ccd=1.39172195\cha=1.47292147\chb=1.08386813\chc=1.0
8356178\chd=1.0838842\che=1.08343161\chf=1.07553226\chg=1.43306793\chh
=1.07606921\cfi=1.07583696\chj=1.0742811\chm=1.07486993\a1=113.485097\
a2=104.20278314\a3=109.23835496\a4=112.04578868\a5=109.86578215\a6=110
.79159335\a7=107.79476246\a8=109.00558803\a9=116.34689078\a10=116.3413
3061\a11=118.794297\a12=118.86493581\a13=121.14960804\a14=121.13200788
\dih1=185.55823225\dih2=177.38324193\dih3=63.74914502\dih4=183.8115888
8\dih5=-57.51775382\dih6=121.76850779\dih7=-121.87690183\dih8=107.2272
0622\dih9=-114.50724653\dih10=104.93194061\dih11=-105.88355441\dih12=8
6.09165026\dih13=-86.42979817\cna=1.13508244\a18=91.37100257\dih17=179
.796442\cnb=1.14373896\a19=90.86901917\dih18=177.99157314\\Version=IBM
-RS6000-G94RevE.1\HF=-379.1224709\S2=1.084\S2-1=0.\S2A=0.806\RMSD=3.42
0e-09\RMSF=2.242e-05\Dipole=-1.4216178,-0.0310317,0.9451397\PG=C01 [X(
C7H9N2)]\\@

Table S4. Total Energies (Hartrees) Required for the Calculation of Reaction Barriers

Species	E1[a]	E2[b]	E3[c]	ZPVE[d]	Energy[e]
ethylene	-78.28435	-78.34358	-78.32096	0.05122	-78.32997
1F,3X-propyl radicals:					
X = H	-217.01954	-217.17060	-217.07573	0.08313	-217.14528
X = F	-316.03262	-316.23828	-316.09006	0.07629	-316.22091
X = CN	-309.02323	-309.19770	-309.09206	0.08236	-309.18577
1F,3X-propyl + ethylene Transition Structure:					
X = H	-295.29262	-295.50359	-295.38778	0.13618[f]	-295.46522
X = F	-394.30591	-394.57140	-394.40231	0.12916	-394.54115
X = CN	-387.29688	-387.53115	-387.40455	0.13536	-387.50609
1CN,3X-propyl radicals:					
X = H	-210.02211	-210.14120	-210.08971	0.08942	-210.12111
X = F	-309.03522	-309.20873	-309.10405	0.08253	-309.19663
X = CN	-302.02417	-302.16675	-302.10429	0.08870	-302.15989
1CN,3X-propyl + ethylene Transition Structure:					
X = H	-288.29585	-288.47629	-288.39673	0.14297	-288.43698
X = F	-387.30847	-387.54360	-387.41073	0.13597	-387.51252
X = CN	-380.29919	-380.50301	-380.41235	0.14221	-380.47672

[a] RMP2/6-31G(d)//HF/6-31G(d) [b] RMP2/6-311G(d,p)//HF/6-31G(d) [c] QCISD(T)/6-31G(d)//HF/6-31G(d) [d] Calculated using B3-LYP/6-31G(d) frequencies [e] Including ZPVE, scaled by 0.9806. [f] Calculated for the gauche addition transition structure.

Table S5. Geometries of Species Involved in the Calculation of IE and EA

1F-propyl radical //MP2/6-31G(d)

1\1\GINC-VPP11\FOpt\UMP2-FU\6-31G(d)\C3H6F1(2)\MLC501\10-Jun-1998\0\\#
N GEOM=ALLCHECK GUESS=READ MP2(FULL)/6-31G(D) OPT=RCFC\\CH3CH2CHF radi
cal (Richard's)\\0,2\C,-0.5497702603,0.2725218665,-0.6923925129\C,-0.5
461546276,0.2762587315,0.7916783526\C,0.8652340537,0.2735326405,-1.284
909707\H,-1.0906245994,-0.6147799371,-1.0395470134\H,-1.1099918887,1.1
474986183,-1.0371376745\H,-0.3379514162,1.1736242636,1.3683471778\F,0.
0288383176,-0.8284366011,1.346118163\H,0.831227001,0.239920093,-2.3768
116835\H,1.4203589512,-0.5964572999,-0.9290781831\H,1.411582099,1.1722
442407,-0.9870928865\\Version=Fujitsu-VP-Unix-G94RevE.2\HF=-216.482064
2\MP2=-217.036482\PUHF=-216.4847258\PMP2-0=-217.0381443\S2=0.759\S2-1=
0.752\S2A=0.75\RMSD=6.864e-09\RMSF=1.652e-06\Dipole=-0.0373506,0.46614
78,-0.3997698\PG=C01 [X(C3H6F1)]\\@

1F-propyl anion //MP2/6-31G(d)

1\1\GINC-PC\FOpt\RMP2-FU\6-31G(d)\C3H6F1(1-)\MLC501\14-Jun-1998\0\\#N
GEOM=ALLCHECK GUESS=READ MP2(FULL)/6-31G(D) OPT=RCFC\\CH3CH2CHF anion
1 (Richard's)\\-1,1\C,-0.6466707855,-0.5319996711,0.4054446743\C,0.096
6196897,0.6967636924,0.9239673917\C,-0.7724518881,-0.6743512399,-1.121
0930914\H,-0.1572597686,-1.4461882067,0.7831643453\H,-1.6556183582,-0.
5254969284,0.8520920192\H,-0.408329823,1.5504153158,0.3980407359\F,1.3
920615135,0.6160587089,0.1384964566\H,-1.2233586068,-1.6234971598,-1.4
545608165\H,0.2280512232,-0.5896608645,-1.5505414136\H,-1.3770203841,0
.1474227739,-1.5245768277\\Version=SGI-G94RevE.2\HF=-216.4104121\MP2=-
216.9946631\RMSD=8.018e-09\RMSF=2.944e-06\Dipole=-0.682964,-0.8912887,
-1.246156\PG=C01 [X(C3H6F1)]\\@

1F,3F-propyl radical //MP2/6-31G(d)

1\1\GINC-PC\FOpt\UMP2-FU\6-31G(d)\C3H5F2(2)\MLC501\11-Jun-1998\0\\#N G
EOM=ALLCHECK GUESS=READ MP2(FULL)/6-31G(D) OPT=RCFC\\1f 3f-propyl radi
cal opp\\0,2\C,-0.8535315854,0.0148860212,-0.5286457041\C,-0.841140191
1,0.0042654072,0.9556492728\C,0.5512593655,0.0188118306,-1.1091731514\
H,-1.3928643588,-0.8652540577,-0.8901379839\H,-1.3838338616,0.90576473
93,-0.8860768139\F,-0.2551561223,1.1071466646,1.4993123864\H,-0.633090
7984,-0.8955104134,1.5243825239\H,0.534172528,0.0229747581,-2.20289422
09\F,1.2129542613,-1.1380162039,-0.6885587362\H,1.1159077067,0.8820712
729,-0.749038861\\Version=SGI-G94RevE.2\HF=-315.3297152\MP2=-316.05261
64\PUHF=-315.3323662\PMP2-0=-316.0542717\S2=0.759\S2-1=0.752\S2A=0.75\
RMSD=5.289e-09\RMSF=3.171e-06\Dipole=-0.4220229,0.0771058,-0.5364031\P
G=C01 [X(C3H5F2)]\\@

1F,3F-propyl anion //MP2/6-31G(d)

1\1\GINC-PC\FOpt\RMP2-FU\6-31G(d)\C3H5F2(1-)\MLC501\14-Jun-1998\0\\#N
GEOM=ALLCHECK GUESS=READ MP2(FULL)/6-31G(D) OPT=RCFC\\1f 3f-propyl rad
ical anti\\-1,1\C,-0.7799987078,-0.2691578984,-0.0860417188\C,-0.75861
99075,-0.25741953,1.448272502\C,0.590002139,-0.2701390292,-0.720879407
6\H,-1.3332439351,-1.1589036273,-0.4235944189\H,-1.3240157972,0.608667
6979,-0.4654575138\F,0.1141667605,0.9502830209,1.7233049832\H,-0.05297
3915,-1.0872029326,1.7159112783\F,0.5652596317,-0.168621333,-2.1502527
494\H,1.124475056,-1.197724243,-0.4836998747\H,1.1626199199,0.58050665
97,-0.3487378286\\Version=SGI-G94RevE.2\HF=-315.2721394\MP2=-316.02490
95\RMSD=2.920e-09\RMSF=1.674e-05\Dipole=0.9691136,-0.2183733,-1.640919
8\PG=C01 [X(C3H5F2)]\\@

1F,3CN-propyl radical //MP2/6-31G(d)

1\1\GINC-PC\FOpt\UMP2-FU\6-31G(d)\C4H5F1N1(2)\MLC501\16-Jun-1998\0\\#N
GEOM=ALLCHECK GUESS=READ MP2(FULL)/6-31G(D) OPT=RCFC\\NCCH2CH2CHF rad
ical (Richard's)\\0,2\C,-1.0787847066,-0.2981328615,-0.4707167894\C,-1
.0584875557,-0.2706807366,1.0124475388\C,0.340776731,-0.3068197183,-1.
0752969332\H,-1.5965327873,-1.2023254194,-0.8089703543\H,-1.6382035985

,0.566130968,-0.8395033074\H,-0.8849597444,0.6371817485,1.5812701923\F
,-0.450197735,-1.3557220976,1.5634960098\C,1.066857378,0.9231703125,-0
.7572781835\H,0.8969033788,-1.1602019007,-0.6769102184\H,0.29292452,-0
.4203612373,-2.1628575311\N,1.6227823951,1.9279789632,-0.4884895236\\V
ersion=SGI-G94RevE.2\HF=-308.2093543\MP2=-309.0535205\PUHF=-308.212078
7\PMP2-0=-309.0552307\S2=0.76\S2-1=0.752\S2A=0.75\RMSD=2.706e-09\RMSF=
6.437e-06\Dipole=-0.8462257,-0.7619242,-0.6103211\PG=C01 [X(C4H5F1N1)]
\\@

1F,3CN-propyl anion //MP2/6-31G(d)

1\1\GINC-RSCQC9\FOpt\UMP2-FC\6-31G(d)\C4H5F1N1(1-)\MICHELLE\22-Jun-199
4\0\\#N UMP2/6-31G* OPT MAXDISK=1048576000\\NCCH2CH2CHF anion 1 (Richa
rd's)\\-1,1\C,-0.8686786505,0.2590150518,0.3093337821\C,-0.8555603099,
0.2297279359,1.8266989694\C,0.5512304329,0.2626271069,-0.3426707254\H,
-1.3995448467,-0.6153591204,-0.0962664208\H,-1.4173813442,1.1506523187
,-0.0285094214\H,-0.2167223615,1.10145318,2.1171413606\F,0.0870918348,
-0.9187833342,2.0973695988\C,0.5727420564,0.1568729621,-1.801645486\H,
1.0865148859,-0.5769037567,0.1083076696\H,1.0722488014,1.1807361622,-0
.047744196\N,0.5275224539,0.0827161262,-2.9827935173\\Version=IBM-RS60
00-G94RevE.1\HF=-308.1653641\MP2=-309.0147053\PUHF=-308.1653641\PMP2-0
=-309.0147053\S2=0.\S2-1=0.\S2A=0.\RMSD=7.750e-09\RMSF=3.342e-05\Dipol
e=0.9987765,0.3171907,-1.1352336\PG=C01 [X(C4H5F1N1)]\\@

1CN-propyl radical //MP2/6-31G(d)

1\1\GINC-VPP10\FOpt\UMP2-FU\6-31G(d)\C4H6N1(2)\MLC501\01-Jul-1998\1\\#
N UMP2=FULL/6-31G(D) OPT=(MAXCYCLE=1000,Z-MATRIX) MAXDISK=1572864000\\
1CN-propyl (Rich) Rad\\0,2\C\C,1,r1\C,1,r2,2,tha1\H,1,r3,2,tha2,3,dih1
,0\H,1,r4,2,tha3,3,-dih2,0\H,2,r5,1,tha4,3,dih3,0\C,2,r6,1,tha5,3,-dih
4,0\X,7,1.,2,90.,1,0.,0\N,7,r7,8,tha6,2,dih5,0\H,3,r8,1,tha7,2,dih6,0\
H,3,r9,1,tha8,10,dih7,0\H,3,r10,1,tha9,10,-dih8,0\\r1=1.49229372\r2=1.
5263106\r3=1.0951212\r4=1.10041794\r5=1.08363285\r6=1.41624913\r7=1.14
804892\r8=1.09236074\r9=1.09329519\r10=1.09235624\tha1=112.26621898\th
a2=109.32371379\tha3=108.94939663\tha4=120.79086445\tha5=121.31377729\
tha6=89.23355962\tha7=110.55884824\tha8=110.92771615\tha9=110.92575336
\dih1=123.13160602\dih2=121.68506849\dih3=29.07166417\dih4=157.1904373
5\dih5=180.36604281\dih6=181.89665496\dih7=119.6881533\dih8=119.992053
53\\Version=Fujitsu-VP-Unix-G94RevE.2\HF=-209.3806596\MP2=-210.0320463
\PUHF=-209.3954488\PMP2-0=-210.0442738\S2=0.89\S2-1=0.839\S2A=0.762\RM
SD=6.792e-09\RMSF=1.328e-05\Dipole=1.2546163,0.5531687,-1.0325152\PG=C
01 [X(C4H6N1)]\\@

1CN-propyl anion //MP2/6-31G(d)

1\1\GINC-VPP10\SP\RMP2-FU\6-31G(d)\C4H6N1(1-)\MLC501\02-Jul-1998\0\\#N
MP2=FULL/6-31G* MAXDISK=1572864000\\1CN-propyl ANION (Rich Rad)\\-1,1
\C\C,1,1.50956454\C,1,1.54264618,2,116.40984093\H,1,1.09112804,2,109.6
3932935,3,122.43930263,0\H,1,1.09491061,2,110.1291844,3,-122.24638783,
0\H,2,1.0824698,1,116.14691527,3,64.5593621,0\C,2,1.39112234,1,119.245
57355,3,-80.33415518,0\X,7,1.,2,90.,1,0.,0\N,7,1.1610576,8,90.49989093
,2,177.55763823,0\H,3,1.09450856,1,112.65065979,2,181.16922827,0\H,3,1
.08877705,1,110.51760398,10,120.4419996,0\H,3,1.08674478,1,110.3771186
9,10,-120.96295975,0\\Version=Fujitsu-VP-Unix-G94RevE.2\HF=-209.357983
\MP2=-210.055601\RMSD=5.450e-09\PG=C01 [X(C4H6N1)]\\@

1CN,3F-propyl radical //MP2/6-31G(d)

1\1\GINC-VPP11\FOpt\UMP2-FU\6-31G(d)\C4H5F1N1(2)\MLC501\30-Jun-1998\1\
\#N UMP2=FULL/6-31G(D) OPT=(MAXCYCLE=1000,Z-MATRIX) MAXDISK=1572864000
\\3CN-1F-propyl Rad3\\0,2\C\C,1,r1\C,1,r2,2,tha1\H,1,r3,2,tha2,3,dih1,
0\H,1,r4,2,tha3,3,-dih2,0\H,2,r5,1,tha4,3,dih3,0\C,2,r6,1,tha5,3,-dih4
,0\X,7,1.,2,90.,1,0.,0\N,7,r7,8,tha6,2,dih5,0\H,3,r8,1,tha7,2,dih6,0\F
,3,r9,1,tha8,10,dih7,0\H,3,r10,1,tha9,10,-dih8,0\\r1=1.49134941\r2=1.5
1596542\r3=1.0949708\r4=1.09933154\r5=1.08221106\r6=1.41335592\r7=1.14
819019\r8=1.09339227\r9=1.39796206\r10=1.09320741\tha1=111.19508479\th
a2=110.81197727\tha3=109.56172937\tha4=119.89688586\tha5=121.35525477\

tha6=89.33705679\tha7=111.25750796\tha8=108.40715332\tha9=111.49614056
\dih1=122.45594481\dih2=119.76049139\dih3=37.55031258\dih4=148.0587895
4\dih5=180.60563317\dih6=184.58805844\dih7=118.82422443\dih8=122.46024
501\\Version=Fujitsu-VP-Unix-G94RevE.2\HF=-308.2280831\MP2=-309.048103
6\PUHF=-308.2431796\PMP2-0=-309.0605876\S2=0.893\S2-1=0.841\S2A=0.762\
RMSD=1.850e-09\RMSF=9.719e-05\Dipole=0.7737989,0.2155739,-1.2326428\PG
=C01 [X(C4H5F1N1)]\\@

1CN,3F-propyl anion //MP2/6-31G(d)

1\1\GINC-VPP11\FOpt\RMP2-FU\6-31G(d)\C4H5F1N1(1-)\MLC501\10-Jul-1998\1
\\#N MP2=FULL/6-31G(D) OPT=(MAXCYCLE=1000,CALCFC,Z-MATRIX) SCF=(QC,DIR
ECT) MAXDISK=1572864000\\1CN-3F-propyl ANION (Rad2)\\-1,1\C\C,1,r1\C,1
,r2,2,tha1\H,1,r3,2,tha2,3,dih1,0\H,1,r4,2,tha3,3,-dih2,0\H,2,r5,1,tha
4,3,dih3,0\C,2,r6,1,tha5,3,-dih4,0\X,7,1.,2,90.,1,0.,0\N,7,r7,8,tha6,2
,dih5,0\F,3,r8,1,tha7,2,dih6,0\H,3,r9,1,tha8,10,dih7,0\H,3,r10,1,tha9,
10,-dih8,0\\r1=1.50685965\r2=1.51531488\r3=1.0991881\r4=1.1006024\r5=1
.09095605\r6=1.39597997\r7=1.19925955\r9=1.09562126\r8=1.4269855\r10=1
.09387838\tha1=112.24851408\tha2=111.07099994\tha3=111.20433674\tha4=1
15.3648682\tha5=117.327792\tha6=90.57909477\tha7=112.7357922\tha8=110.
49465919\tha9=110.24887488\dih1=120.66995604\dih2=121.12958756\dih3=70
.59025698\dih4=70.41890564\dih5=176.97171409\dih7=119.60366037\dih6=18
1.53304183\dih8=119.91202669\\Version=Fujitsu-VP-Unix-G94RevE.2\HF=-30
8.2142174\MP2=-309.0879117\RMSD=0.000e+00\RMSF=7.850e-05\Dipole=0.5571
427,1.2710578,-1.9589224\PG=C01 [X(C4H5F1N1)]\\@

1CN,3CN-propyl radical //MP2/6-31G(d)

1\1\GINC-VPP10\FOpt\UMP2-FU\6-31G(d)\C5H5N2(2)\MLC501\30-Jun-1998\1\\#
N UMP2=FULL/6-31G(D) OPT=(MAXCYCLE=1000,Z-MATRIX) MAXDISK=1572864000\\
3CN 1CN-propyl (Rich) Rad3\\0,2\C\C,1,r1\C,1,r2,2,tha1\H,1,r3,2,tha2,3
,dih1,0\H,1,r4,2,tha3,3,-dih2,0\H,2,r5,1,tha4,3,dih3,0\C,2,r6,1,tha5,3
,dih4,0\X,7,1.,2,90.,1,0.,0\N,7,r7,8,tha6,2,dih5,0\C,3,r8,1,tha7,2,dih
6,0\H,3,r9,1,tha8,10,dih7,0\H,3,r10,1,tha9,10,-dih8,0\X,10,1.,3,90.,1,
180.,0\N,10,r11,13,tha10,3,dih9,0\\r1=1.49241373\r2=1.53719715\r3=1.09
376619\r4=1.09923288\r5=1.08411114\r6=1.41344663\r7=1.14770539\r8=1.46
336676\r9=1.09437912\r10=1.09451203\r11=1.17945301\tha1=112.20974796\t
ha2=110.22525891\tha3=109.53373259\tha4=120.54854908\tha5=120.90314883
\tha6=89.09227731\tha7=111.36436283\tha8=110.21779459\tha9=109.8925587
9\tha10=92.18501581\dih1=121.70572479\dih2=120.95710116\dih3=43.791160
74\dih4=216.99487085\dih5=180.55649571\dih6=-58.1903348\dih7=120.88811
051\dih8=120.89272061\dih9=179.46586581\\Version=Fujitsu-VP-Unix-G94Re
vE.2\HF=-301.1058555\MP2=-302.0470277\PUHF=-301.1211352\PMP2-0=-302.05
96732\S2=0.895\S2-1=0.843\S2A=0.763\RMSD=4.632e-09\RMSF=4.173e-05\Dipo
le=0.2650698,-0.2969856,-1.3778491\PG=C01 [X(C5H5N2)]\\@

1CN,3CN-propyl anion //MP2/6-31G(d)

1\1\GINC-VPP09\FOpt\UMP2-FU\6-31G(d)\C5H5N2(1-)\MLC501\09-Jul-1998\1\\
#N UMP2=FULL/6-31G(D) OPT=(MAXCYCLE=1000,CALCFC,Z-MATRIX) MAXDISK=1572
864000\\3CN 1CN-propyl ANION (Rich Rad3)\\-1,1\C\C,1,r1\C,1,r2,2,tha1\
H,1,r3,2,tha2,3,dih1,0\H,1,r4,2,tha3,3,-dih2,0\H,2,r5,1,tha4,3,dih3,0\
C,2,r6,1,tha5,3,dih4,0\X,7,1.,2,90.,1,0.,0\N,7,r7,8,tha6,2,dih5,0\C,3,
r8,1,tha7,2,dih6,0\H,3,r9,1,tha8,10,dih7,0\H,3,r10,1,tha9,10,-dih8,0\X
,10,1.,3,90.,1,180.,0\N,10,r11,13,tha10,3,dih9,0\\r1=1.49593053\r2=1.5
6300819\r3=1.0992733\r4=1.09931511\r5=1.09105357\r6=1.39752327\r7=1.19
840521\r8=1.46530572\r9=1.09457447\r10=1.0948457\r11=1.18198106\tha1=1
13.79380536\tha2=111.36911481\tha3=110.91177691\tha4=115.27633337\tha5
=116.11233292\tha6=89.66990941\tha7=114.33966573\tha8=107.92687834\tha
9=108.71250112\tha10=93.14661538\dih1=120.48261448\dih2=121.44761963\d
ih3=74.35160733\dih4=295.42945299\dih5=177.38136377\dih7=-122.21011464
\dih6=181.28111064\dih8=238.12619461\dih9=179.39089566\\Version=Fujits
u-VP-Unix-G94RevE.2\HF=-301.1039634\MP2=-302.098411\PUHF=-301.1039634\
PMP2-0=-302.098411\S2=0.\S2-1=0.\S2A=0.\RMSD=9.159e-09\RMSF=5.645e-05\
Dipole=0.5080753,1.2599622,-1.5166074\PG=C01 [X(C5H5N2)]\\@

Table S6. Total Energies (Hartrees) Required for the Calculation of IE and EA

Species	ZPVE[a]	E1[b]	E2[c]	E3[d]	G2(MP2)[e]
1F-propyl					
Radical	0.08887	-217.17079	-217.30149	-217.23371	-217.34524
Anion	0.08592	-217.14859	-217.30172	-217.21245	-217.35387
Cation	0.08887[f]	-216.86510	-216.98933	-216.92886	-217.03374
1F,3F-propyl					
Radical	0.08214	-316.23867	-316.42939	-316.30293	-316.49551
Anion	0.07934	-316.22906	-316.44247	-316.29424	-316.51681
Cation	0.08214[f]	-315.92224	-316.10564	-315.98794	-316.17300
1F,3CN-propyl					
Radical	0.08875	-309.20109	-309.38427	-309.27482	-309.45894
Anion	0.08608	-309.20447	-309.40936	-309.27898	-309.49201
Cation	0.08875[f]	-308.87627	-309.05216	-308.95121	-309.1278
1CN-propyl					
Radical	0.09438	-210.12831	-210.25304	-210.21347	-210.31911
Anion	0.09405	-210.16897	-210.31409	-210.23923	-210.37037
Cation	0.09438[f]	-209.80814	-209.92707	-209.88432	-209.98398
1CN,3F-propyl					
Radical	0.08762	-309.19586	-309.38002	-309.28271	-309.46882
Anion	0.08732	-309.25126	-309.45600	-309.32243	-309.53420
Cation	0.08762[f]	-308.86861	-309.04628	-308.94647	-309.12591
1CN,3CN-propyl					
Radical	0.09428	-302.15657	-302.33348	-302.25290	-302.43082
Anion	0.09400	-302.22307	-302.41955	-302.30348	-302.50603
Cation	0.09428[f]	-301.82197	-301.99241	-301.90914	-302.08040

[a] Calculated using HF/6-31G(d) frequencies [b] MP2/6-311G(d,p)//MP2/6-31G(d) [c] MP2/6-311+G(3df,2p)//MP2/6-31G(d) [d] QCISD(T)/6-311G(d,p)//MP2/6-31G(d) [e] G2(MP2) Energy = E3 + E2 - E1 + Higher Level Correction Term + scaled (by 0.8929) ZPVE (see reference 30) [f] Approximated as the ZPVE of the corresponding radical with the same geometry.