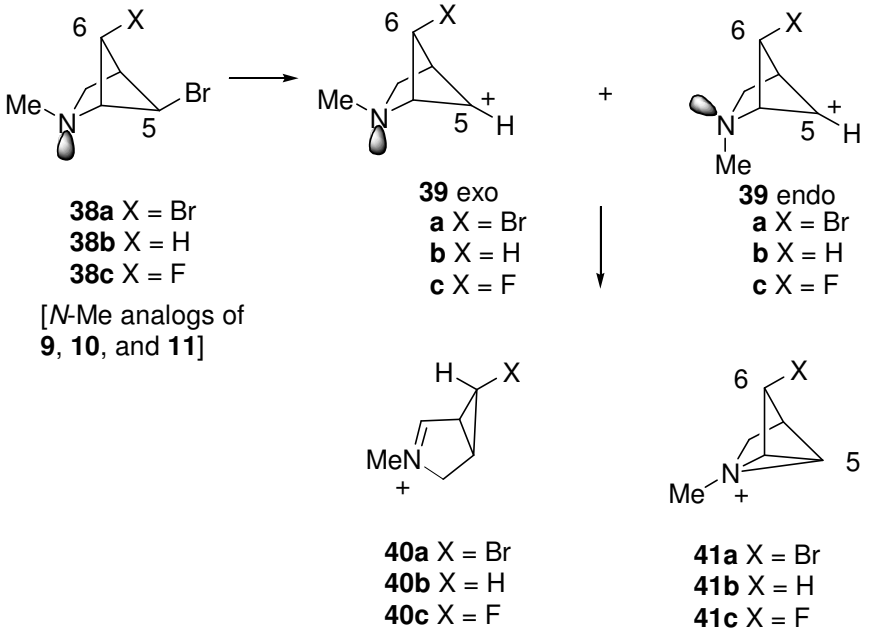
5(6)-*anti*-Substituted-2-azabicyclo[2.1.1]hexanes. The Nucleophilic Displacement Route

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Computational Methods employed for Ions Derived from Cations 39. (ms. reference 27).



The cation was sketched as shown (above left) with the tetrahedral nitrogen lone pair oriented toward the carbon from which the leaving group departed (*exo*) as well as in the other (*endo*) configuration. The cationic carbon was labeled C5, while the substituted carbon was labeled C6. Each optimization led to an iminium ion **40**; *exo* and *endo* isomers of cation **39** led to the same ions. Geometries were optimized with the (1) Hartree-Fock 6-31+G(d,p)[1] and (2) B3LYP/6-31+G(d,p)[2] methods/basis sets using the Gaussian 03 suite of computations[3]. The energies tabulated below have been corrected for zero point energies themselves unscaled.

Hartree Fock/6-31+G(d,p). Energies[1] were corrected for unscaled zero point energies.

Structure	Energy	zpe	Energy (corr)
X=Br **40a**	-2856.567192	0.153086	-2856.414106
X=H **40b**	-287.252802	0.163437	-287.089365
X=F **40c**	-386.092078	0.155186	-385.936891

[1] Energies are in Hartrees (1 Hartree = 627.51 kcal/mol); [2] Energy of the initial structure was calculated to be about 92-97 kcal/mol higher than the geometry optimized structure.

B3LYP/6-31+G(d,p). Energies[1] were corrected for unscaled zero point energies.

Structure	Energy	zpe	Energy (corr)
X=Br **40a**	-2860.270481	0.142426	-2860.128055
X=H **40b**	-289.158289	0.152471	-289.005818
X = F **40c**	-388.383334[2]	0.144325	-388.239009
	-388.314232[3]	0.144549	-388.169684

[1] Energies are in Hartrees (1 Hartree = 627.51 kcal/mol);[2] iminium ion; [3] aziridinium ion.
The energy difference between the aziridium and iminium ions is calculated to be 43.5 kcal/mol.

Coordinates for the ions prior to optimizations.

endo-5-ion-*anti*-6-Br **39a**

N	0.072899	0.369393	1.141979
C	-0.215761	-0.443328	2.422139
C	1.034578	-0.137246	3.230828
C	2.065573	-0.519850	2.207221
C	1.493213	0.685180	1.522587
H	-0.220667	-1.498558	2.245037
H	-1.155385	-0.171501	2.855865
H	1.074208	-0.527528	4.226322
H	2.053138	-1.481709	1.738636
C	1.252737	1.331093	2.910784
H	1.218918	2.292562	3.379116
H	2.057212	1.155654	0.744475
C	-0.603660	1.673920	1.104862
H	-1.299119	1.738210	1.915481
H	0.122238	2.454858	1.194907
H	-1.126560	1.778245	0.177181
Br	3.865629	-0.288916	2.802677

exo-5-ion-*anti*-6-Br **39a**

N	-0.057216	0.504725	1.215796
C	-0.340440	-0.275246	2.517657
C	1.025624	-0.205322	3.178955
C	1.815682	-0.795944	2.001011
C	1.430087	0.571248	1.435958
H	-0.551511	-1.310179	2.346596
H	-1.163608	0.151073	3.052022
H	1.097318	-0.564132	4.184447
H	2.324230	-1.693062	1.715603
C	1.521353	1.153281	2.835231
H	0.975517	2.033807	3.102883
H	1.966514	1.022340	0.627463
C	-0.504762	1.903930	1.268986
H	-1.085686	2.059185	2.154041
H	0.347519	2.550690	1.283747
H	-1.101884	2.120383	0.407886
Br	3.306573	1.486146	3.427084

endo-5-ion **39b**

N	0.077849	0.369097	1.141447
C	-0.212675	-0.444686	2.420510
C	1.031184	-0.130105	3.235904
C	2.070257	-0.506707	2.218258
C	1.493982	0.694215	1.529701
H	-0.209837	-1.500033	2.244057
H	-1.156407	-0.178629	2.848861
H	1.067805	-0.519525	4.231851
H	3.075954	-0.370671	2.557325
H	2.066580	-1.468909	1.750224
C	1.241694	1.339409	2.916134
H	1.199123	2.300923	3.383658
H	2.059251	1.167827	0.754418
C	-0.606842	1.669236	1.099758
H	-1.307173	1.729554	1.906478
H	0.113527	2.454867	1.193316
H	-1.125259	1.769646	0.169134

exo-5-ion **39b**

N	-0.061779	0.504977	1.217441
C	-0.341309	-0.274419	2.520444
C	1.029221	-0.212764	3.173270
C	1.808567	-0.806907	1.989975
C	1.427219	0.562899	1.428382
H	-0.559305	-1.308003	2.349909
H	-1.158705	0.156127	3.060253
H	1.105138	-0.572778	4.178022
H	2.310235	-1.706663	1.700718
C	1.530493	1.143285	2.827504
H	0.991334	2.026673	3.099226

H	1.961149	1.011592	0.616906
C	-0.501047	1.906651	1.274489
H	-1.075560	2.064485	2.163265
H	0.354963	2.548562	1.284434
H	-1.102282	2.127172	0.417291
H	2.533677	1.323826	3.152971

endo-5-ion-*anti*-F **39c**

C	1.671585	0.853272	-0.685521
N	0.645967	0.598712	0.323622
C	1.460993	-0.339795	1.203657
C	2.539641	-0.803391	0.198778
C	2.034188	-0.496901	-1.220769
H	1.955503	0.170481	2.003643
H	0.848079	-1.108989	1.625055
H	3.504632	-1.197548	0.440299
H	1.286112	-1.125745	-1.656471
C	2.886893	0.761964	0.123619
H	3.629649	1.426541	0.512916
H	1.447050	1.651203	-1.362123
C	0.107371	1.734723	1.085391
H	-0.579215	1.375831	1.823427
H	0.909649	2.253668	1.567000
H	-0.400358	2.401562	0.420233
F	3.028194	-0.426548	-2.131540

exo-5-ion-*anti*-F **39c**

C	1.656287	0.853212	-0.652247
N	0.611142	0.647692	0.371743
C	1.471962	-0.318753	1.211268
C	2.519611	-0.803375	0.198780
C	1.989215	-0.496892	-1.198987
H	1.992477	0.185658	1.998373
H	0.865425	-1.087803	1.642050
H	3.483687	-1.210725	0.421318
H	1.224735	-1.116087	-1.619784
C	2.885061	0.750721	0.125903
H	3.643988	1.405518	0.500296
H	1.438973	1.651102	-1.331251
F	2.964108	-0.437899	-2.130976
C	-0.519879	0.006275	-0.314025
H	-0.344364	0.007868	-1.369530
H	-0.619767	-1.002178	0.029407
H	-1.418763	0.546252	-0.101116

Coordinates for Ions obtained using HF/6-31+G(d,p) (Method 1) and using B3LYP/6-31+G(d,p) (Method 2)

Iminium ion (X=Br)**40a**(Method 1)

N	-0.090108	-0.043283	-2.432941
C	1.214105	0.171109	-1.754759
C	0.812090	0.640509	-0.368817
C	-0.704129	0.765408	-0.382224
C	-1.084314	0.309999	-1.722985
H	1.767504	0.918322	-2.309096
H	1.770726	-0.757228	-1.756371
H	1.419324	1.373023	0.127659
H	-1.270725	1.534520	0.105997
C	0.001992	-0.301763	0.424581
H	-0.086056	-1.324410	0.107379
H	-2.088160	0.254723	-2.107111
C	-0.146569	-0.594331	-3.790138
H	0.253033	-1.598819	-3.780693
H	-1.170767	-0.609340	-4.130365
H	0.449564	0.028794	-4.442290
Br	-0.027792	-0.156063	2.308044

Iminium ion (X=Br)**40a** (Method 2)

N	-0.088777	-0.045927	2.452713
C	1.218782	0.189155	1.766793
C	0.813442	0.651989	0.374399
C	0.017567	-0.304544	-0.428283
C	-1.102842	0.313864	1.725975
H	1.796140	-0.740503	1.768685
H	1.770222	0.946853	2.332861
H	1.405292	1.411283	-0.124208
H	-0.067900	-1.338136	-0.106297
C	-0.728284	0.763106	0.395145
H	-1.307904	1.518776	-0.121192
H	-2.113499	0.257060	2.121935
C	-0.139015	-0.608073	3.807091
H	0.473246	0.010141	4.468646
H	-1.170122	-0.622209	4.160132
H	0.260621	-1.625181	3.792605
Br	-0.025787	-0.157988	-2.323111

Iminium ion (X=H)**40b** (Method 1)

N	-0.067035	-0.048062	0.953408
C	1.199906	-0.173642	0.188905
C	0.726196	-0.329200	-1.244467
C	-0.787669	-0.400569	-1.189166
C	-1.099470	-0.211223	0.227603
H	1.732754	-1.041678	0.555789
H	1.802547	0.709834	0.355650
H	1.279767	-0.978919	-1.895340
H	-1.405598	-1.042351	-1.787077
C	-0.065488	0.786050	-1.808541
H	-0.099515	1.732164	-1.296389
H	-2.085603	-0.195442	0.658553
C	-0.053150	0.230299	2.391390
H	0.383899	1.204596	2.560582
H	-1.063094	0.210744	2.772060
H	0.541016	-0.525524	2.886082
H	-0.138887	0.852725	-2.878100

Iminium ion (X=H) **40b** (Method 2)

N	-0.066588	-0.050680	-0.964087
C	1.205581	-0.184812	-0.190739
C	0.735162	-0.332100	1.249302
C	-0.049702	0.793651	1.819933
C	-1.115629	-0.215599	-0.218144
H	1.822519	0.702178	-0.363734
H	1.739256	-1.063482	-0.566787
H	1.279238	-1.002846	1.904464
H	-0.083362	1.749614	1.304254
C	-0.803105	-0.395417	1.190034
H	-1.431798	-1.021438	1.812000
H	-2.109807	-0.208021	-0.657785
C	-0.052902	0.237618	-2.402608
H	0.562141	-0.511494	-2.907496
H	-1.070615	0.206399	-2.791821
H	0.375622	1.228885	-2.570907
H	-0.133511	0.854928	2.899745

Iminium ion (X=F)**40c** (Method 1)

C	-1.094812	-0.258959	-0.654812
N	-0.078442	-0.004771	-1.376606
C	1.209260	-0.182266	-0.655481
C	0.772311	-0.508256	0.760356
C	-0.020674	0.513720	1.457908
H	1.755299	-0.989764	-1.125754
H	1.786781	0.729807	-0.733773
H	1.344748	-1.203934	1.344610
H	-0.080919	1.531808	1.116935
C	-0.751233	-0.592050	0.727864
H	-1.345090	-1.288218	1.288962
H	-2.089698	-0.217557	-1.063106

C	-0.096413	0.402355	-2.785287
H	0.333609	1.390162	-2.873780
H	0.490559	-0.303338	-3.356689
H	-1.114163	0.411276	-3.144425
F	-0.071406	0.413987	2.786664

Aziridinium ion (X=F)**41c** from ***endo*** (Method 2)

C	0.000000	0.000000	0.000000
N	0.000000	0.000000	1.526427
C	1.431745	0.000000	2.003328
C	1.744092	0.893374	0.788682
C	1.473810	-0.049665	-0.413959
H	1.473302	0.523850	2.960078
H	1.887151	-0.991385	2.069585
H	2.581319	1.585260	0.777941
H	2.006054	-1.000773	-0.488310
C	0.209247	1.269793	0.746465
H	-0.387662	2.162813	0.887636
H	-0.886587	-0.393634	-0.484027
C	-1.182556	-0.403296	2.309952
H	-1.175665	-1.489072	2.424615
H	-1.135604	0.082869	3.286136
H	-2.086522	-0.090184	1.784814
F	1.598526	0.626212	-1.608225

The following was drawn as an iminium ion and minimized.

iminium ion (X=F)**40c** from ***exo*** (Method 2)

C	-1.112506	-0.263359	-0.650966
N	-0.078152	-0.002575	-1.391601
C	1.214110	-0.195931	-0.662297
C	0.776409	-0.518066	0.759584
C	-0.003582	0.519971	1.466854
H	1.760827	-1.012720	-1.144065
H	1.808730	0.719206	-0.740761
H	1.338809	-1.235187	1.347780
H	-0.067621	1.549603	1.121828
C	-0.769431	-0.592955	0.719705
H	-1.376920	-1.268651	1.310925
H	-2.115228	-0.222909	-1.068376
F	-0.067089	0.418604	2.816433
C	-0.092783	0.413266	-2.799221
H	-1.117598	0.416451	-3.170158
H	0.334457	1.415342	-2.886130
H	0.512103	-0.288111	-3.379683

The following were drawn as aziridinium ions and minimized.

Aziridinium ion (X=Br) **41a** (Method 1)

C	1.325413	-0.298301	1.831217
N	-0.135888	-0.067712	2.010218
C	-0.817576	-0.195855	0.666274
C	-0.136587	1.046094	1.032365
C	1.173914	0.392744	0.471285
H	1.858347	0.291934	2.563324
H	1.628496	-1.335819	1.863998
H	-1.858770	-0.453214	0.683276
H	-0.470708	2.038413	1.263704
C	0.276710	-0.593815	-0.301985
H	0.581693	-1.626276	-0.361163
H	1.993375	0.903802	-0.001579
C	-0.880899	-0.153550	3.272404
H	-0.349650	0.407615	4.027891
H	-1.866954	0.266007	3.131972
H	-0.960057	-1.191887	3.561868
Br	-0.150012	-0.000300	-2.075262

Aziridinium ion (X=Br)**41a** (Method 2)

C	1.337867	-0.293783	1.849397
N	-0.138335	-0.065614	2.037001
C	-0.825814	-0.210198	0.661679
C	-0.141556	1.053514	1.030284
C	1.181491	0.389544	0.474525
H	1.873325	0.312967	2.582553
H	1.646789	-1.341040	1.893129
H	-1.876679	-0.474860	0.686045
H	-0.482726	2.057086	1.254885
C	0.279505	-0.606161	-0.302818
H	0.589110	-1.648900	-0.371408
H	2.009352	0.903289	-0.004307
C	-0.886269	-0.149490	3.303523
H	-0.357267	0.429792	4.062945
H	-1.887455	0.260566	3.159330
H	-0.954410	-1.196953	3.604244
Br	-0.150373	0.001623	-2.092170

Aziridinium ion (X=H) **41b** (Method 1)

C	1.312866	-0.317304	-0.034005
N	0.043646	-0.072053	0.703545
C	-1.113429	-0.169699	-0.269220
C	-0.317325	1.055805	-0.185129
C	0.653110	0.391142	-1.221551
H	2.097906	0.256612	0.438052
H	1.587472	-1.358678	-0.131103
H	-2.062732	-0.404039	0.172442
H	-0.508852	2.048999	0.171980
C	-0.504859	-0.564582	-1.600576
H	-0.269962	-1.604493	-1.786147
H	1.240315	0.905385	-1.961819
C	-0.146839	-0.164694	2.154553
H	0.648162	0.377241	2.646849
H	-1.100739	0.270015	2.417493
H	-0.125022	-1.205848	2.444176
H	-1.113218	-0.164836	-2.401165

Aziridinium ion (X=H)**41b** (Method 2)

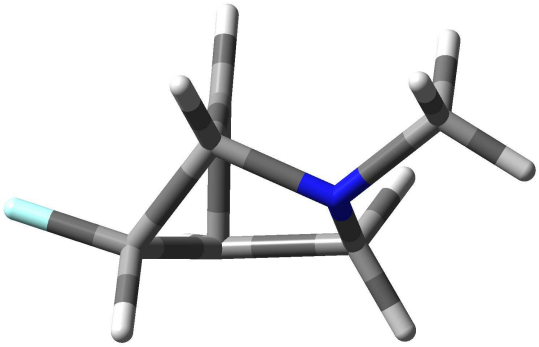
C	1.324814	-0.320882	-0.031130
N	0.045392	-0.070929	0.717687
C	-1.127176	-0.171624	-0.282414
C	-0.316665	1.069539	-0.191963
C	0.662497	0.388111	-1.229680
H	2.115460	0.262907	0.444579
H	1.601561	-1.373936	-0.122965
H	-2.084791	-0.408242	0.167702
H	-0.510200	2.075013	0.163487
C	-0.508300	-0.568757	-1.612675
H	-0.278685	-1.619594	-1.804692
H	1.260032	0.900952	-1.977307
C	-0.152636	-0.165841	2.173479
H	0.641438	0.389697	2.676227
H	-1.122109	0.262140	2.434700
H	-0.122248	-1.217668	2.465392
H	-1.113403	-0.158053	-2.424636

Aziridinium ion (X=F)**41c** (Method 1)

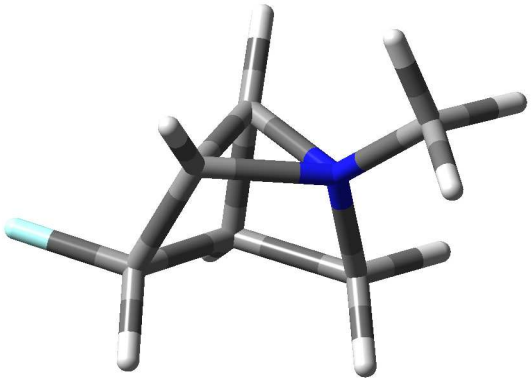
C	1.361809	-0.320065	0.654684
N	-0.051727	-0.069172	1.061509
C	-0.933946	-0.177903	-0.148550
C	-0.187123	1.057547	0.108563
C	1.014793	0.396753	-0.652359
H	2.013407	0.244896	1.305560
H	1.643719	-1.364009	0.624583
H	-1.965448	-0.418651	0.022255
H	-0.471603	2.049357	0.400211

C	-0.007947	-0.554224	-1.296570
H	0.260429	-1.584622	-1.476929
H	1.754834	0.903039	-1.247106
C	-0.589235	-0.164880	2.425215
H	0.072568	0.365596	3.094654
H	-1.572367	0.282906	2.451626
H	-0.650394	-1.207179	2.704283
F	-0.519241	-0.023389	-2.428399

The exception in these optimizations of secondary cations **39** occurred with the *endo*-5-ion-6-*anti*-F **39c** and is illustrated below:



endo-5-cation-*anti*-6-F **39c**



41c ion optimized at the B3LYP/6-31+G(d,p) level

The following table provides additional basis for comparing the (uncorr.) energies for cations calculated as geometry optimizations, and where optimizations led to alternate structures, single point energy calculations.

Method 1 (MP2/6-31+G(d,p)//HF/6-31G(d)				Method 2 (B3LYP/6-31+G(d,p)//HF/6-31G(d)			
X	**39**[a]	**40**[b]	**41**[c]	X	**39**	**40**	**41**
a	-2856.420501	-2856.567192	-2856.498289	**a**	-2860.122236	-2860.270481	-2860.202732
Br	(92.1)	(0.0)	(43.2)	Br	(93.0)	(0.0)	(42.5)
b	-287.092322	-287.252802	-287.180735	**b**	-289.001012	-289.158289	-289.088453
H	(100.7)	(0.0)	(45.2)	H	(94.9)	(0.0)	(43.8)
c	-385.943860	-386.092078	-386.022956	**c**	-388.229360	-388.383334	-388.314232
F	(93.0)	(0.0)	(43.4)	F	(96.6)	(0.0)	(43.4)

[a] *endo*-5-ion (single point energy); [b] iminium ion(geometry opt.); [c] aziridinium ion (geometry opt.).

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