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

Charge Transfer Limit of a Chemical Adduct: The Role of Perturbation on External Potential

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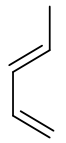
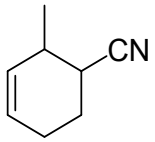
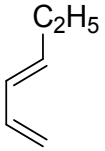
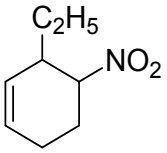
Table of Contents

Table S1: 11 donor-acceptor pairs and the corresponding adducts

S.No.	Donor (B)	Acceptor (A)	Adduct (AB)
1	 (*E*)-penta-1,3-diene	 acrylonitrile	 2-methylcyclohex-3-enecarbonitrile
2	 (*E*)-hexa-1,3-diene	 nitroethene	 3-ethyl-4-nitrocyclohex-1-ene
3	$(CH_3)_2$-NH dimethylamine	BH_3 borane	$(CH_3)_2$-NH-BH_3
4	(CH3)3-N trimethylamine	BH_3 borane	$(CH_3)_3$-N-BH_3
5	CH_3-NH_2 methanamine	BH_2F fluoroborane	CH_3-NH_2-BH_2F
6	$(CH_3)_3N$ trimethylamine	BH_2F fluoroborane	$(CH_3)_3N$-BH_2F
7	CH_3-NH_2 methanamine	BHF_2 difluoroborane	CH_3-NH_2-BHF_2
8	$(CH_3)_2$-NH dimethylamine	BHF_2 difluoroborane	$(CH_3)_2$-NH-BHF_2
9	$(CH_3)_3$-N trimethylamine	BHF_2 difluoroborane	$(CH_3)_3$-N-BHF_2
10	$(CH_3)_2$-NH dimethylamine	BF_3 trifluoroborane	$(CH_3)_2$-NH-BF_3
11	$(CH_3)_3$-N trimethylamine	BF_3 trifluoroborane	$(CH_3)_3$-N-BF_3

Optimized Coordinates (in Angstroms) of:

(1) buta-1,3-diene

Table S2:

	ATOM	X	Y	Z
1	C	-3.398660	3.865639	0.241773
2	C	-4.252544	3.148058	0.967702
3	C	-4.017393	2.666713	2.325109
4	C	-2.851092	2.245297	2.808754
5	H	-3.629509	4.170759	-0.769672
6	H	-2.439856	4.172065	0.640877
7	H	-5.225503	2.920952	0.543487
8	H	-4.888286	2.646564	2.974098
9	H	-1.964351	2.197205	2.189023
10	H	-2.752334	1.932624	3.839553

(2) penta-1,3-diene:

Table S3:

	ATOM	X	Y	Z
1	C	-5.538530	3.364702	0.197702
2	C	-5.437316	3.154017	1.510901
3	C	-4.984961	1.910905	2.091822
4	C	-4.824853	1.695242	3.399943
5	C	-4.333761	0.421166	3.990361
6	H	-5.296096	2.586065	-0.515546
7	H	-5.870552	4.310043	-0.207049
8	H	-5.685674	3.952798	2.202314
9	H	-4.759921	1.106627	1.396592
10	H	-5.049521	2.500250	4.094011
11	H	-4.174342	-0.339937	3.225262
12	H	-5.045270	0.021201	4.719467
13	H	-3.390950	0.563796	4.526065

(3) hexa-1,3-diene:

Table S4:

	ATOM	X	Y	Z
1	C	-5.222622	4.332271	0.015738
2	C	-5.968058	3.491077	0.727314
3	C	-5.798440	2.043962	0.810610
4	C	-4.631109	1.396729	0.782279
5	C	-4.428633	-0.083549	0.856669
6	C	-5.682507	-0.931665	0.869545
7	H	-4.410013	3.979936	-0.608119
8	H	-5.401619	5.399288	0.027530
9	H	-6.803029	3.897888	1.289553
10	H	-6.712030	1.471679	0.934719
11	H	-3.722787	1.988688	0.722064
12	H	-3.826107	-0.305631	1.745010
13	H	-3.794454	-0.386158	0.016121
14	H	-5.437337	-1.992442	0.917499
15	H	-6.279353	-0.769246	-0.029349
16	H	-6.315256	-0.701501	1.728017

(4) acrylaldehyde:

Table S5:

	ATOM	X	Y	Z
1	C	-3.137298	3.423200	-0.255089
2	C	-3.648722	3.028538	1.058727
3	C	-4.548831	2.058567	1.189778
4	O	-2.336835	4.313342	-0.440897
5	H	-3.540935	2.823677	-1.103723
6	H	-3.270516	3.579755	1.918226
7	H	-4.928416	1.509088	0.328669
8	H	-4.945352	1.766769	2.160587

(5) acrylonitrile:

Table S6:

	ATOM	X	Y	Z
1	C	-0.103692	-0.167871	-0.218337
2	C	-0.294905	0.388712	-1.410128
3	C	-0.704915	1.730942	-1.618995
4	N	-1.067967	2.795253	-1.874694
5	H	0.181842	-1.213009	-0.143164
6	H	-0.252552	0.390547	0.701577
7	H	-0.144988	-0.190718	-2.320247

(6) nitroethene:

Table S7:

	ATOM	X	Y	Z
1	C	-0.498637	0.964216	1.015838
2	C	-1.304231	1.772294	0.355715
3	N	-1.635110	1.558491	-1.044589
4	O	-1.175883	0.587582	-1.625162
5	O	-2.378828	2.394248	-1.542904
6	H	-0.042596	0.107240	0.528021
7	H	-0.288156	1.143752	2.067083
8	H	-1.808405	2.641302	0.759878

(7) borane:

Table S8:

	ATOM	X	Y	Z
1	B	-0.496954	1.679149	-2.543563
2	H	-1.097231	0.944625	-3.278479
3	H	-1.097000	2.414206	-1.809045
4	H	0.703084	1.678692	-2.543260

(8) fluoroborane:

Table S9:

	ATOM	X	Y	z
1	B	-4.242761	1.295988	0.010911
2	F	-3.034610	1.829697	-0.126616
3	H	-4.513460	0.368755	-0.693023
4	H	-4.977757	1.792842	0.809249

(9) difluoroborane:

Table S10:

	ATOM	X	Y	Z
1	B	-7.761826	1.798934	0.000083
2	H	-7.812007	0.612657	0.000044
3	F	-6.595156	2.424817	-0.000135
4	F	-8.858396	2.539734	0.000354

(10) trifluoroborane:

Table S11:

	ATOM	X	Y	Z
1	B	-2.359117	1.710997	-0.002532
2	F	-1.259763	1.135274	-0.447501
3	F	-3.515947	1.082970	-0.081447
4	F	-2.298973	2.915061	0.531098

(11) ammonia:

Table S12:

	ATOM	X	Y	Z
1	N	-4.301945	1.577230	0.503714
2	H	-4.613023	1.873157	-0.414423
3	H	-4.612678	2.292495	1.150893
4	H	-3.290141	1.631256	0.489550

(12) methanamine:

Table S13:

	ATOM	X	Y	Z
1	C	-4.293085	0.801418	0.033553
2	N	-3.033616	1.527312	0.043593
3	H	-4.098354	-0.271725	0.026881
4	H	-4.837813	1.028766	-0.883591
5	H	-4.967349	1.010064	0.875993
6	H	-2.514118	1.319918	0.886899
7	H	-3.200364	2.525393	0.049981

(13) dimethylamine:

Table S14:

	ATOM	X	Y	Z
1	N	-3.952074	0.843632	0.263242
2	C	-4.253812	-0.546526	-0.024196
3	C	-5.077327	1.726840	0.012986
4	H	-3.401157	-1.170664	0.242434
5	H	-4.426257	-0.666051	-1.096503
6	H	-5.141120	-0.933312	0.501698
7	H	-5.994606	1.451457	0.557042
8	H	-5.309729	1.715909	-1.054246
9	H	-4.813332	2.750161	0.277692
10	H	-3.655625	0.933017	1.226163

(14) trimethylamine:

Table S15:

	ATOM	X	Y	Z
1	N	-4.730219	2.153484	0.286020
2	C	-3.606791	2.950340	-0.171639
3	C	-5.999315	2.783475	-0.027564
4	C	-4.671322	0.805570	-0.245489
5	H	-3.591308	3.078400	-1.268801
6	H	-2.672799	2.469498	0.121906
7	H	-3.637139	3.937705	0.288728
8	H	-6.814447	2.194708	0.394492
9	H	-6.170002	2.878843	-1.114490
10	H	-6.032507	3.779558	0.413032
11	H	-4.724281	0.776183	-1.349119
12	H	-5.495329	0.211052	0.149873
13	H	-3.740040	0.326006	0.058173

Table S16. Changes in $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and ΔE values with respect to charge transfer (ΔN) for Diels-Alder pair acrylonitrile (CH_2=CH-CN, A) and penta-1,3-diene (CH_2=CH-CH=CH-CH_3, B).

S.No.	ΔN	$\Delta E_{B(A)}$ (kJ mol^{-1})	$\Delta E_{A(B)}$ (kJ mol^{-1})	ΔE (kJ mol^{-1})
1	0.00000	000.000	0000.000	0000.000
2	0.01929	006.478	-009.153	-002.675
3	0.03929	013.387	-018.414	-005.027
4	0.05929	020.492	-027.444	-006.952
5	0.07929	027.794	-036.243	-008.449
6	0.09929	035.293	-044.811	-009.518
7	0.11929	042.988	-053.148	-010.160
8*	0.13929	050.75	-061.12	-010.370
9	0.15929	058.969	-069.129	-010.160
10	0.17929	067.254	-076.772	-009.518
11	0.19929	075.737	-084.185	-008.448
12	0.21929	084.416	-091.367	-006.951
13	0.23929	093.291	-098.318	-005.027
14	0.25929	102.364	-105.038	-002.674
15	0.27859	111.302	-111.302	-000.000

* The ΔN_{eqlm} value is 0.139 (when $\Delta E = \Delta E_{SE(AB)}$ i.e., the most negative)

Table S17. Change in $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and ΔE values with respect to the charge transfer (ΔN) for Diels-Alder pair nitroethene (CH_2=$CHNO_2$, A) and hexa-1,3-diene (CH_2=CH-CH=CH-C_2H_5, B).

S. No.	ΔN	$\Delta E_{B(A)}$ (kJ mol^{-1})	$\Delta E_{A(B)}$ (kJ mol^{-1})	ΔE (kJ mol^{-1})
1	0.00000	000.000	0000.000	000.000
2	0.02474	008.250	-013.186	-04.936
3	0.06474	022.217	-033.790	-11.573
4	0.10474	036.963	-053.514	-16.551
5	0.14474	052.488	-072.357	-19.869
6	0.18474	068.793	-090.321	-21.521
7*	0.205	77.33	-99.06	-21.73
8	0.22474	085.876	-107.405	-21.529
9	0.26474	103.739	-123.609	-19.870
10	0.30474	122.382	-138.933	-16.551
11	0.34474	141.803	-153.376	-11.573
12	0.38474	162.004	-166.940	-04.936
13	0.40949	174.891	-174.890	000.000

* The ΔN_{eqlm} value is 0.205 (when $\Delta E = \Delta E_{SE(AB)}$ i.e., the most negative).

Table S18. Changes in $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and ΔE values with respect to charge transfer (ΔN) for borane (BH_3 , A) and dimethylamine [$(CH_3)_2$-NH, B].

S. No.	ΔN	$\Delta E_{B(A)}$ (kJ mol^{-1})	$\Delta E_{A(B)}$ (kJ mol^{-1})	ΔE (kJ mol^{-1})
1	0.00000	0.00000	0.0000	0.00000
2	0.01118	2.25374	-3.3886	-1.13486
3	0.04118	8.69074	-12.2139	-3.52316
4	0.07118	15.69853	-20.65467	-4.95614
5*	0.10118	23.27711	-28.71092	-5.4338
6	0.13118	31.42649	-36.38263	-4.95614
7	0.16118	40.14666	-43.66983	-3.52316
8	0.19118	49.43763	-50.57249	-1.13486
9	0.20236	53.04962	-53.04962	0.00000

* The ΔN_{eqlm} value is 0.10118 (when $\Delta E = \Delta E_{SE(AB)}$ i.e., the most negative).

Table S19. Changes in $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and ΔE values with respect to charge transfer (ΔN) for borane (BH_3 , A) and trimethylamine [$(CH_3)_3$-N, B].

S. No.	ΔN	$\Delta E_{B(A)}$ (kJ mol^{-1})	$\Delta E_{A(B)}$ (kJ mol^{-1})	ΔE (kJ mol^{-1})
1	0.00000	0.0000	0.00000	0.00000
2	0.01435	2.0702	-4.33822	-2.26802
3	0.04435	6.78261	-13.12293	-6.34033
4	0.07435	12.01544	-21.52312	-9.50768
5	0.10435	17.76871	-29.53878	-11.77007
6	0.13435	24.0424	-37.16991	-13.12751
7*	0.16435	30.83653	-44.41652	-13.57999
8	0.19435	38.15109	-51.2786	-13.12751
9	0.22435	45.98608	-57.75616	-11.77007
10	0.25435	54.34151	-63.84919	-9.50768
11	0.28435	63.21736	-69.55769	-6.34033
12	0.31435	72.61365	-74.88166	-2.26802
13	0.328706	77.29466	-77.29466	0.00000

* The ΔN_{eqlm} value is 0.16435 (when $\Delta E = \Delta E_{SE(AB)}$ i.e., the most negative).

Table S20. Changes in $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and ΔE values with respect to charge transfer (ΔN) for fluoroborane (BH_2F , A) and methanamine (CH_3 -NH_2, B).

S. No.	ΔN	$\Delta E_{B(A)}$ (kJ mol^{-1})	$\Delta E_{A(B)}$ (kJ mol^{-1})	ΔE (kJ mol^{-1})
1	0.01611	3.80382	-8.63063	-4.82681
2	0.05611	14.00859	-29.20479	-15.1962
3	0.09611	25.29615	-48.55743	-23.26129
4	0.13611	37.66649	-66.68855	-29.02206
5	0.17611	51.11961	-83.59814	-32.47853
6*	0.21611	65.65552	-99.28621	-33.63068
7	0.25611	81.27422	-113.75275	-32.47853
8	0.29611	97.97571	-126.99777	-29.02206
9	0.33611	115.75998	-139.02127	-23.26129
10	0.37611	134.62703	-149.82324	-15.1962
11	0.41611	154.57688	-159.40369	-4.82681
12	0.43222	162.92064	-162.92064	0.00000

* The ΔN_{eqlm} value is 0.21611 (when $\Delta E = \Delta E_{SE(AB)}$ i.e., the most negative).

Table S21. Changes in $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and ΔE values with respect to charge transfer (ΔN) for fluoroborane (BH_2F , A) and trimethylamine [$(CH_3)_3$-N, B].

S. No.	ΔN	$\Delta E_{B(A)}$ (kJ mol^{-1})	$\Delta E_{A(B)}$ (kJ mol^{-1})	ΔE (kJ mol^{-1})
1	0.05948	9.35631	-30.88241	-21.5261
2	0.11948	20.86728	-59.29893	-38.43164
3	0.17948	34.45998	-84.96701	-50.50703
4	0.23948	50.13441	-107.88667	-57.75226
5*	0.29948	67.89056	-128.05789	-60.16734
6	0.35948	87.72843	-145.48069	-57.75226
7	0.41948	109.64804	-160.15506	-50.50703
8	0.47948	133.64936	-172.08101	-38.43164
9	0.53948	159.73242	-181.25852	-21.5261
10	0.59896	187.64488	-187.64488	0.00000

* The ΔN_{eqlm} value is 0.29948 (when $\Delta E = \Delta E_{SE(AB)}$ i.e., the most negative).

Table S22. Changes in $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and ΔE values with respect to charge transfer (ΔN) for difluoroborane (BHF_2, A) and methanamine (CH_3 -NH_2, B).

S. No.	ΔN	$\Delta E_{B(A)}$ (kJ mol^{-1})	$\Delta E_{A(B)}$ (kJ mol^{-1})	ΔE (kJ mol^{-1})
1	0.04314	10.58259	-25.09882	-14.51622
2	0.09314	24.42256	-52.22554	-27.80299
3	0.14314	39.95437	-77.2479	-37.29354
4	0.19314	57.17803	-100.1659	-42.98786
5*	0.24314	76.09355	-120.97953	-44.88597
6	0.29314	96.70093	-139.68879	-42.98786
7	0.34314	119.00015	-156.29369	-37.29354
8	0.39314	142.99123	-170.79422	-27.80299
9	0.44314	168.67416	-183.19039	-14.51622
10	0.48628	192.19294	-192.19294	0.00000

* The ΔN_{eqlm} value is 0.24314 (when $\Delta E = \Delta E_{SE(AB)}$ i.e., the most negative).

Table S23. Changes in $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and ΔE values with respect to charge transfer (ΔN) for difluoroborane (BHF_2, A) and dimethylamine [$(CH_3)_2$ -NH, B].

S. No.	ΔN	$\Delta E_{B(A)}$ (kJ mol^{-1})	$\Delta E_{A(B)}$ (kJ mol^{-1})	ΔE (kJ mol^{-1})
1	0.03232	6.72949	-18.94942	-12.21994
2	0.11232	26.23564	-62.07096	-35.83532
3	0.19232	49.80078	-99.80533	-50.00455
4*	0.27232	77.42489	-132.15252	-54.72763
5	0.35232	109.10798	-159.11253	-50.00455
6	0.43232	144.85004	-180.68537	-35.83532
7	0.51232	184.65109	-196.87103	-12.21994
8	0.54465	201.88698	-201.88698	0.000000

* The ΔN_{eqlm} value is 0.27232 (when $\Delta E = \Delta E_{SE(AB)}$ i.e., the most negative).

Table S24. Changes in $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and ΔE values with respect to charge transfer (ΔN) for difluoroborane (BHF_2, A) and trimethylamine [$(CH_3)_3$-N, B].

S. No.	ΔN	$\Delta E_{B(A)}$ (kJ mol^{-1})	$\Delta E_{A(B)}$ (kJ mol^{-1})	ΔE (kJ mol^{-1})
1	0.02379	3.49727	-14.03508	-10.53781
2	0.08379	13.77011	-47.31197	-33.54186
3	0.14379	26.12468	-77.55858	-51.4339
4	0.20379	40.56097	-104.7749	-64.21393
5	0.26379	57.07899	-128.96094	-71.88195
6*	0.32379	75.67873	-150.11668	-74.43796
7	0.38379	96.3602	-168.24215	-71.88195
8	0.44379	119.12339	-183.33732	-64.21393
9	0.50379	143.96831	-195.40221	-51.4339
10	0.56379	170.89495	-204.43681	-33.54186
11	0.62379	199.90332	-210.44113	-10.53781
12	0.64758	211.98319	-211.98319	0

* The ΔN_{eqlm} value is 0.32379 (when $\Delta E = \Delta E_{SE(AB)}$ i.e., the most negative).

Table S25. Changes in $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and ΔE values with respect to charge transfer (ΔN) for trifluoroborane (BF_3, A) and dimethylamine [$(CH3)_2NH$, B].

S. No.	ΔN	$\Delta E_{B(A)}$ (kJ mol^{-1})	$\Delta E_{A(B)}$ (kJ mol^{-1})	ΔE (kJ mol^{-1})
1	0.03249	6.76577	-19.51961	-12.75385
2	0.11249	26.28035	-63.54746	-37.26712
3	0.19249	49.8539	-101.82898	-51.97508
4*	0.27249	77.48644	-134.36417	-56.87773
5	0.35249	109.17795	-161.15303	-51.97508
6	0.43249	144.92845	-182.19556	-37.26712
7	0.51249	184.73792	-197.49176	-12.75385
8	0.54499	202.06461	-202.06461	0.000000

* The ΔN_{eqlm} value is 0.27249 (when $\Delta E = \Delta E_{SE(AB)}$ i.e., the most negative).

Table S26. Changes in $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and ΔE values with respect to charge transfer (ΔN) for trifluoroborane (BF_3, A) and trimethylamine [$(CH_3)_3$-N, B].

S. No.	ΔN	$\Delta E_{B(A)}$ (kJ mol^{-1})	$\Delta E_{A(B)}$ (kJ mol^{-1})	ΔE (kJ mol^{-1})
1	0.00201	0.28258	-1.23432	-0.95174
2	0.08201	13.43455	-47.4514	-34.01685
3	0.16201	30.28735	-87.92214	-57.63479
4	0.24201	50.84101	-122.64656	-71.80555
5*	0.32201	75.09551	-151.62465	-76.52914
6	0.40201	103.05085	-174.8564	-71.80555
7	0.48201	134.70704	-192.34183	-57.63479
8	0.56201	170.06408	-204.08093	-34.01685
9	0.64201	209.12196	-210.0737	-0.95174
10	0.64401	210.14996	-210.14996	0.00000

* The ΔN_{eqlm} value is 0.32201 (when $\Delta E = \Delta E_{SE(AB)}$ i.e., the most negative).

Figure S1. Plot showing the profiles of $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and ΔE with respect to ΔN for penta-1, 3-diene (B) and acrylonitrile (A).

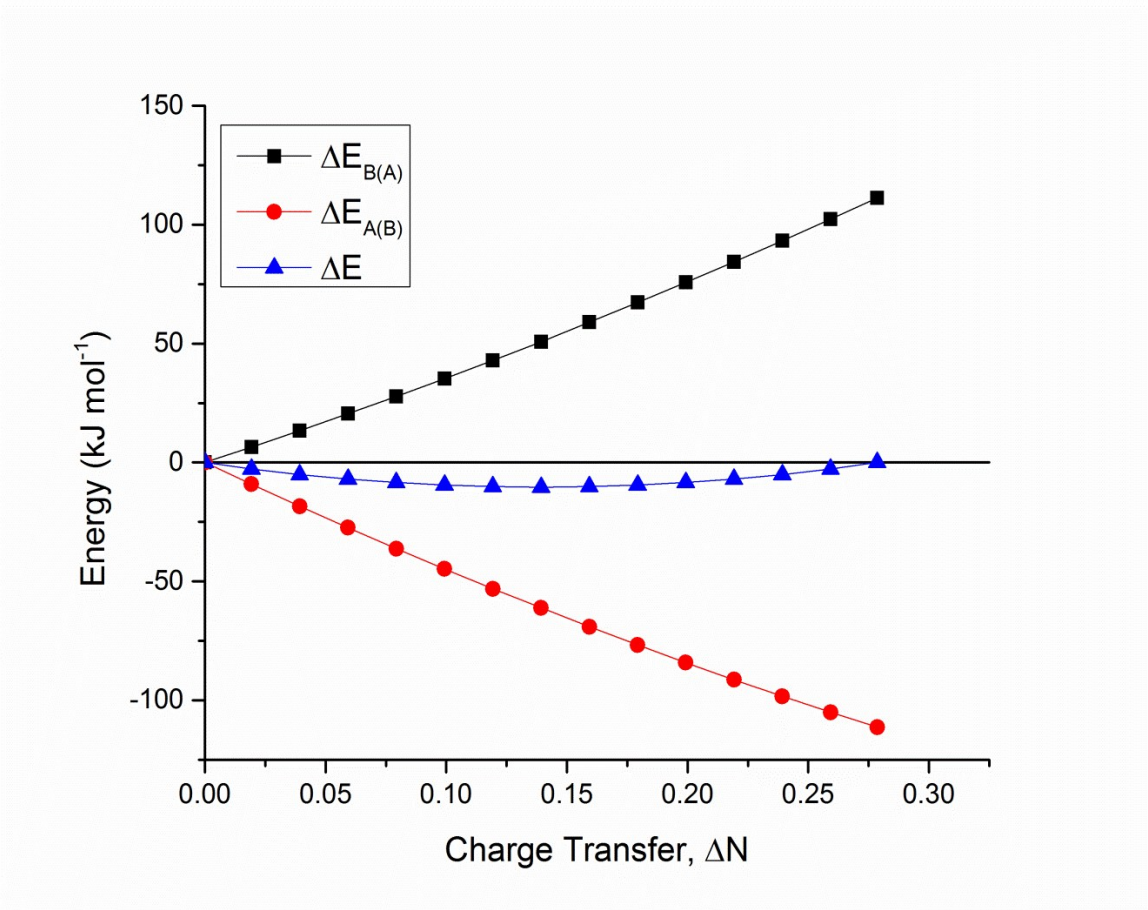


Figure S2. Plot showing the profiles of $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and ΔE with respect to ΔN for hexa-1, 3-diene (B) and nitroethene (A).

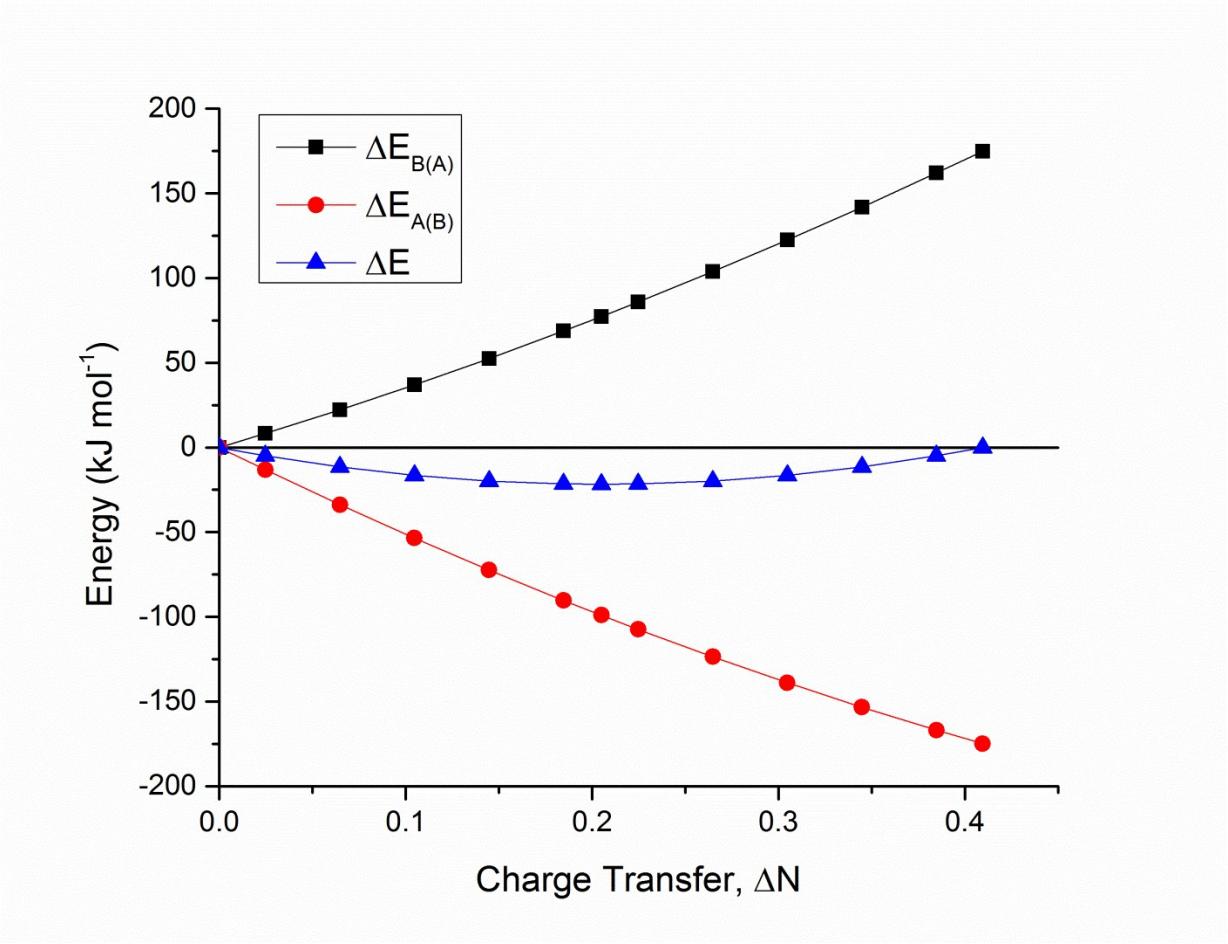

200
150
100
50
0
-50
-100
-150
-200
0.0
0.1
0.2
0.3
0.4
Energy (kJ mol-1)
Charge Transfer, ΔN
ΔEB(A)
ΔEA(B)
ΔE

Figure S3. Plot showing the profiles of $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and ΔE with respect to ΔN for dimethylamine (B) and borane (A).

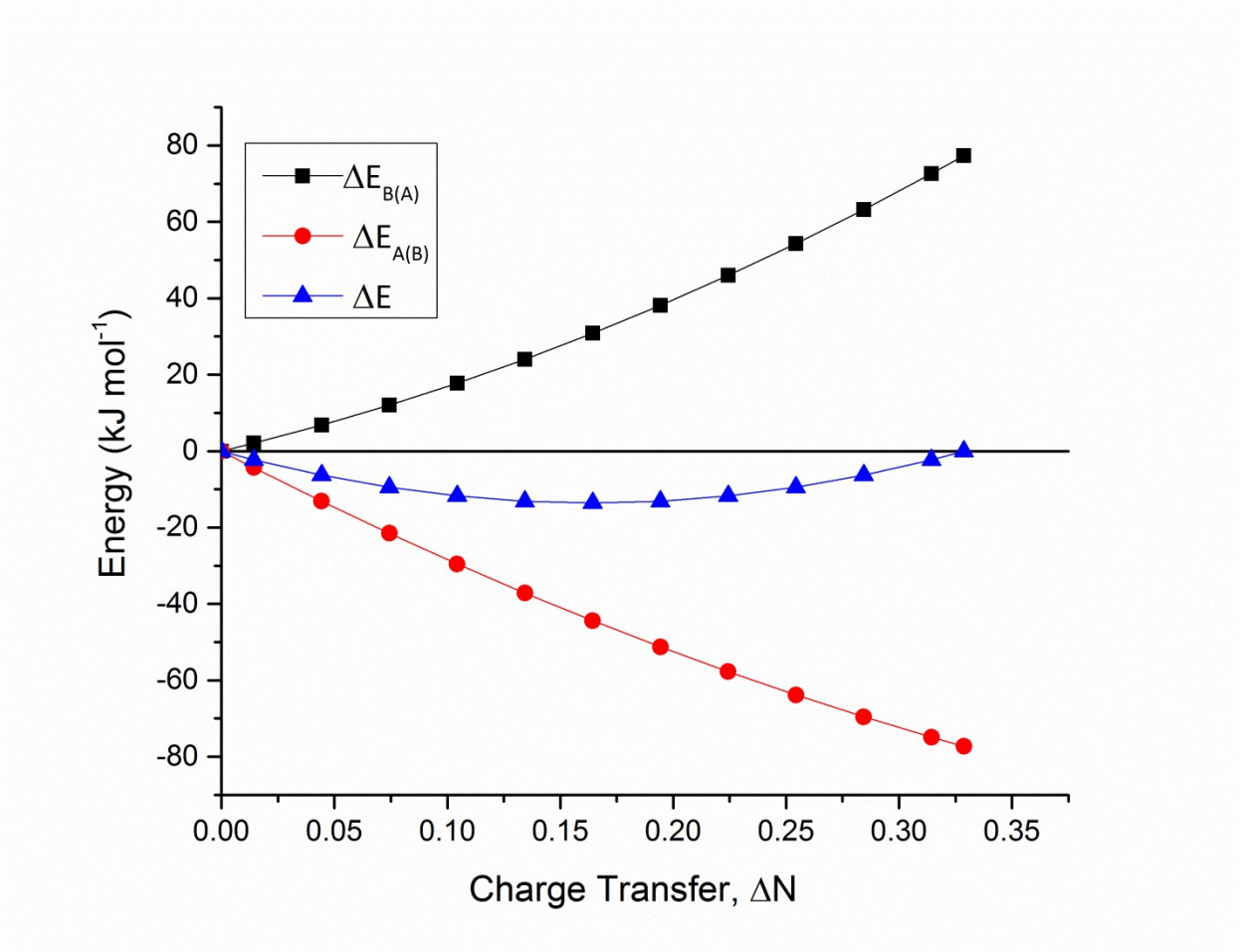


Figure S4. Plot showing the profiles of $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and ΔE with respect to ΔN for trimethylamine (B) and borane (A).

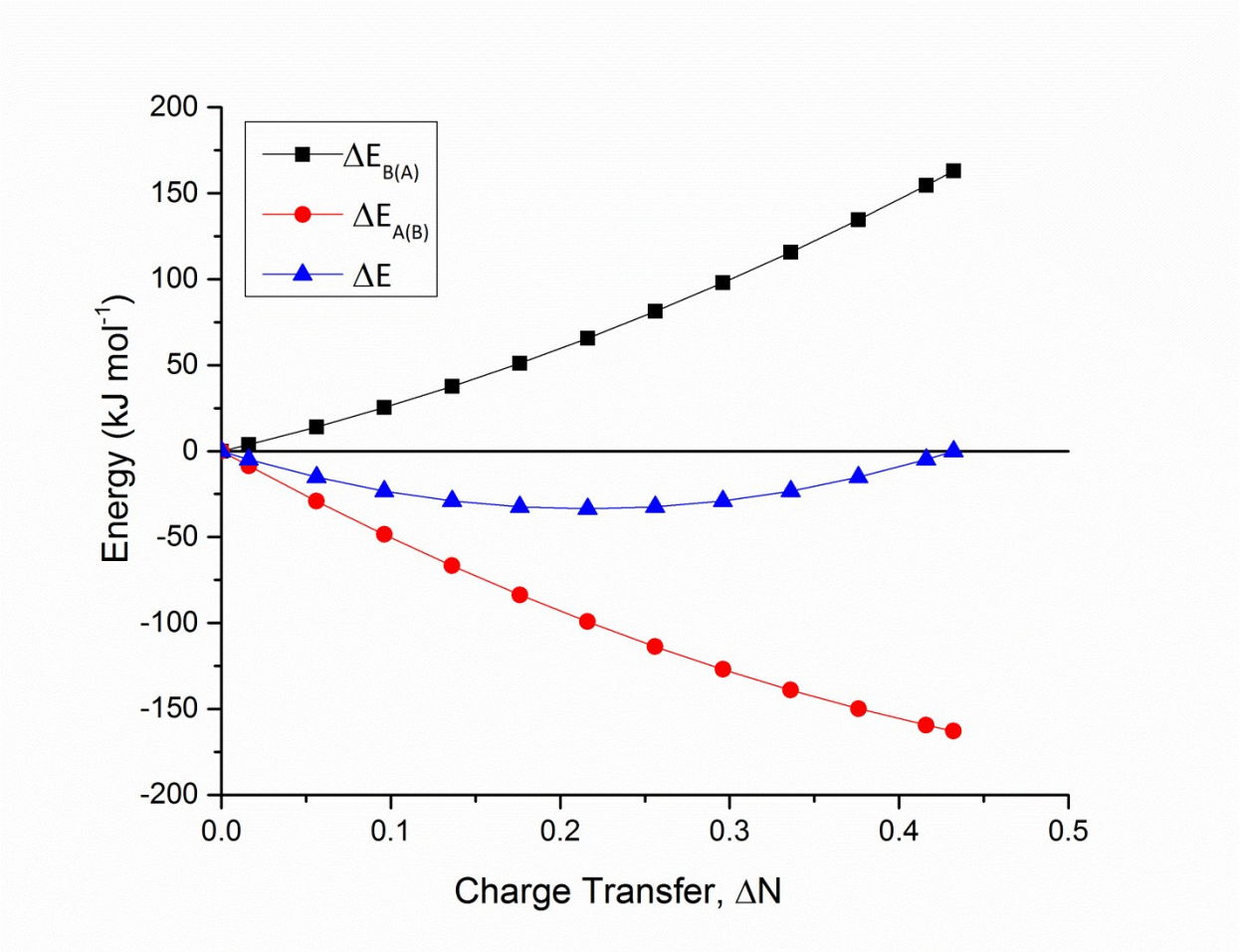


Figure S5. Plot showing the profiles of $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and ΔE with respect to ΔN for methanamine (B) and fluoroborane (A).

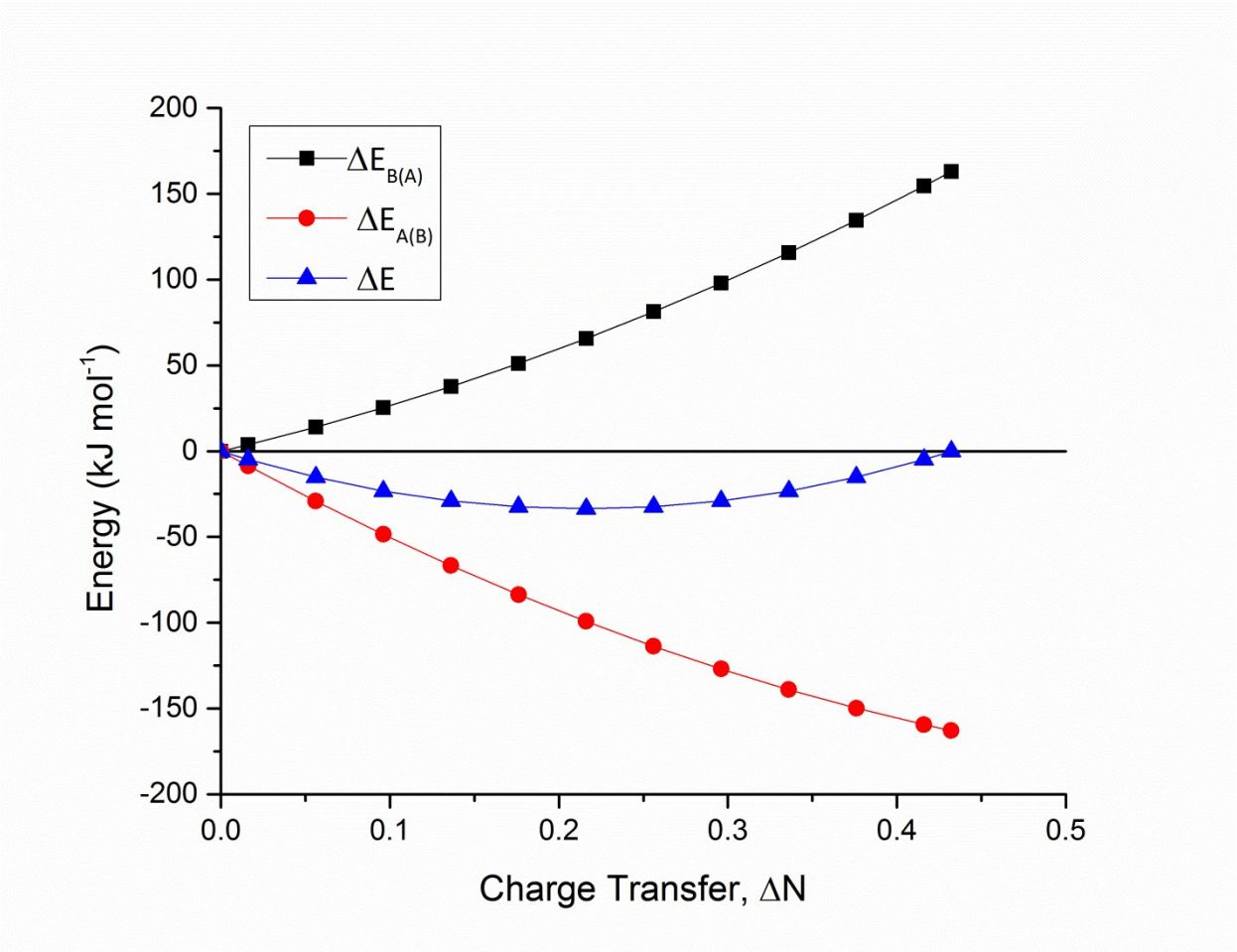


Figure S6. Plot showing the profiles of $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and ΔE with respect to ΔN for trimethylamine (B) and fluoroborane (A).

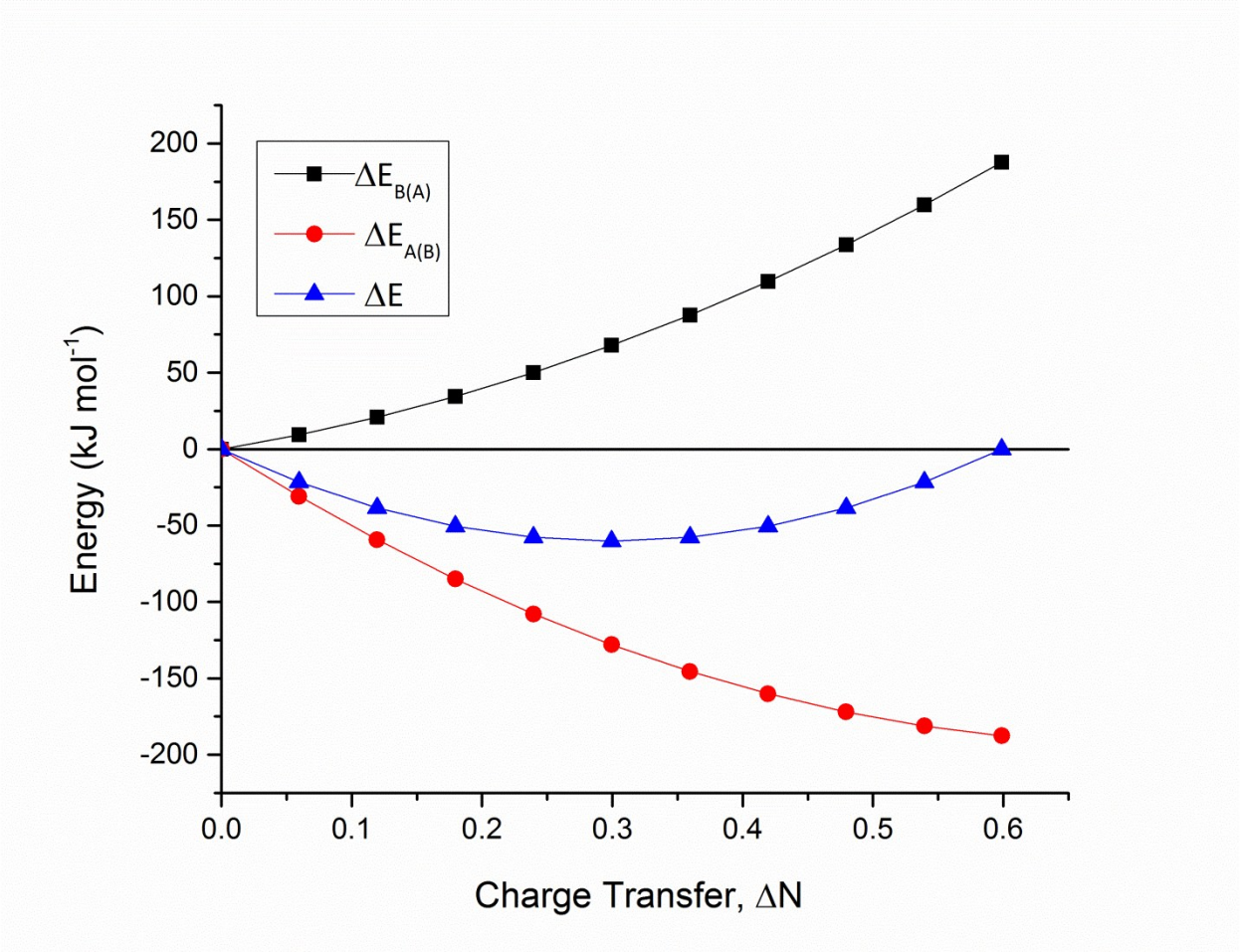


Figure S7. Plot showing the profiles of $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and ΔE values with respect to ΔN for methanamine (B) and difluoroborane (A).

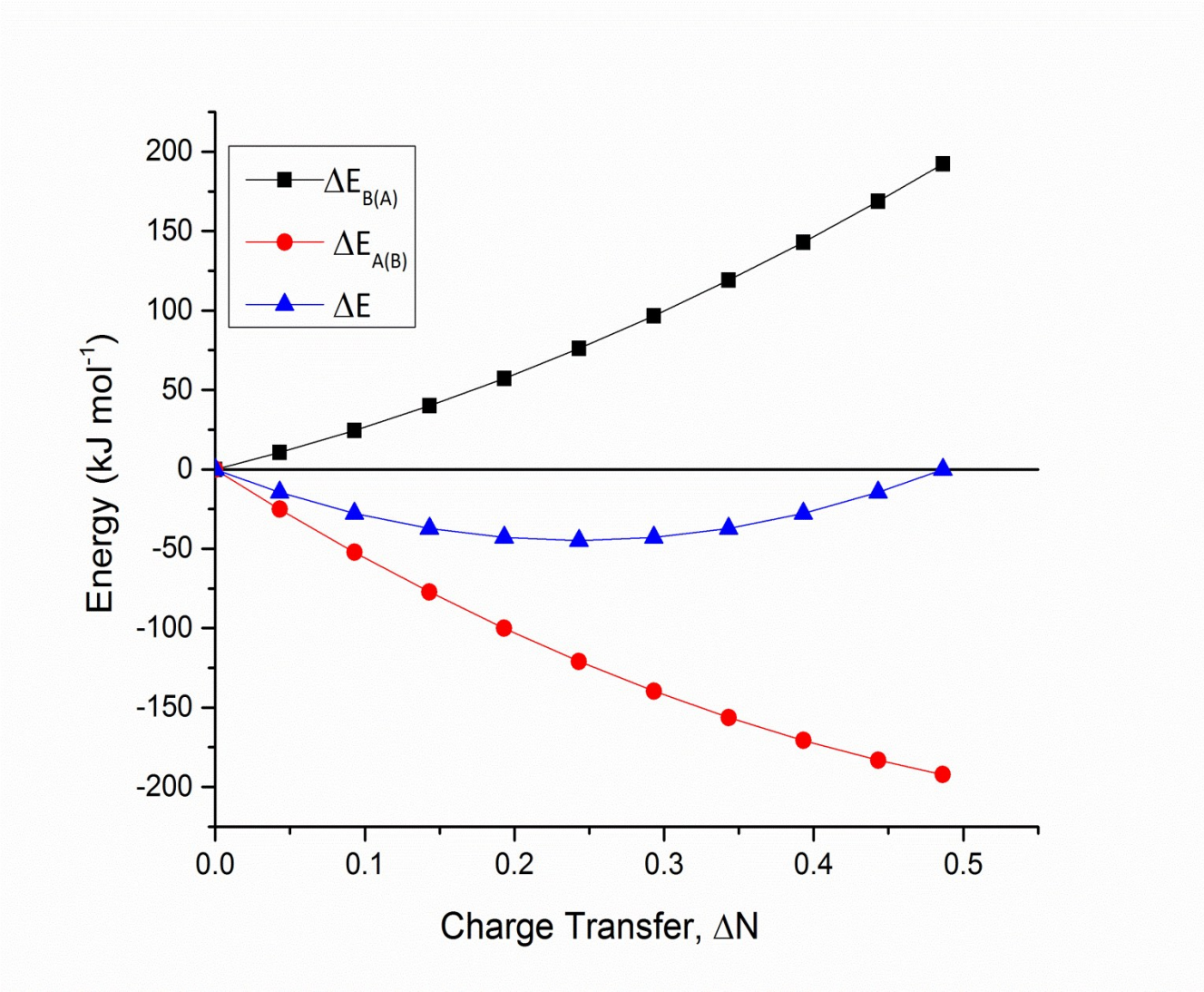


Figure S8. Plot showing the profiles of $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and ΔE with respect to ΔN for dimethylamine (B) and difluoroborane (A)

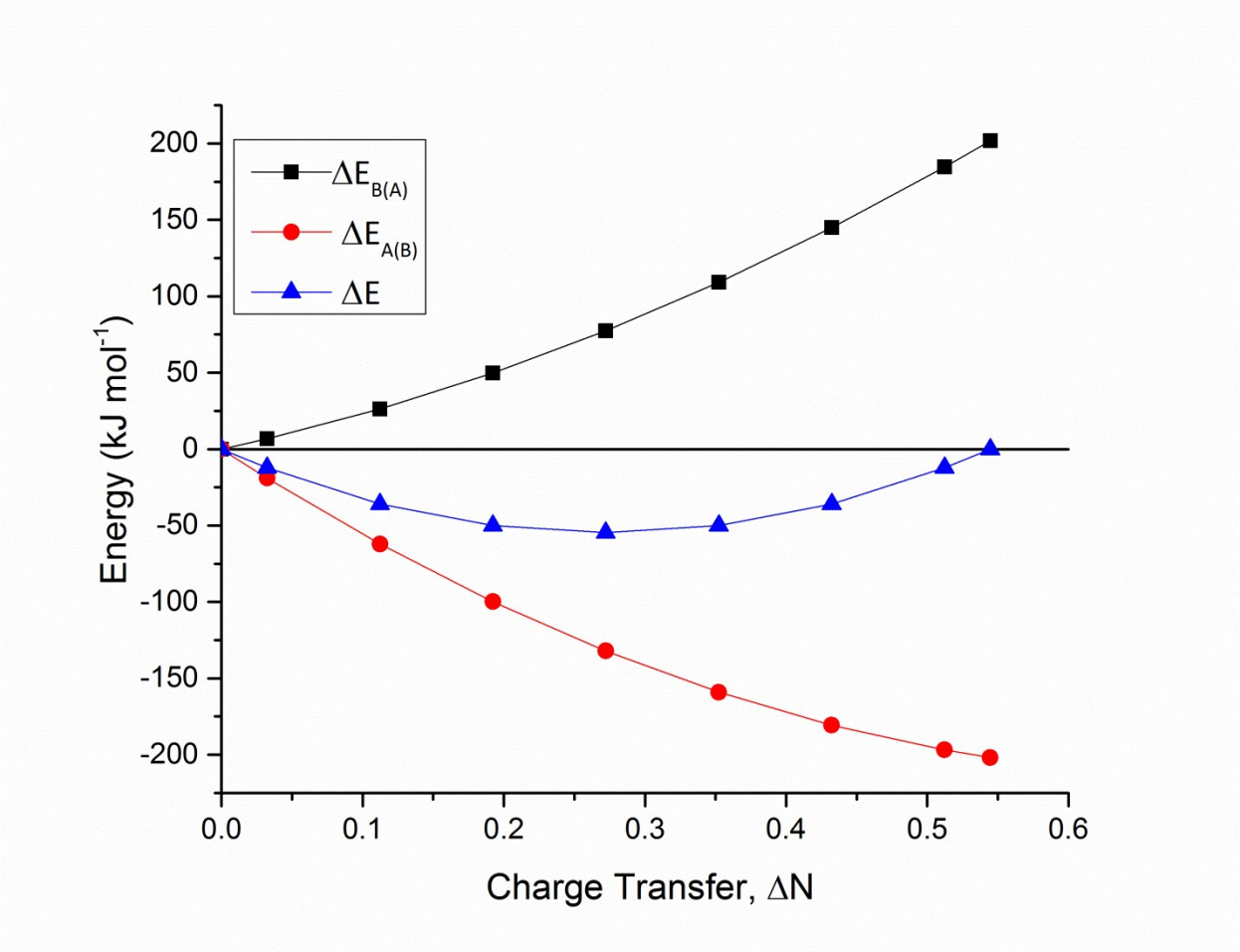


Figure S9. Plot showing the profiles of $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and ΔE with respect to ΔN for trimethylamine (B) and difluoroborane (A).

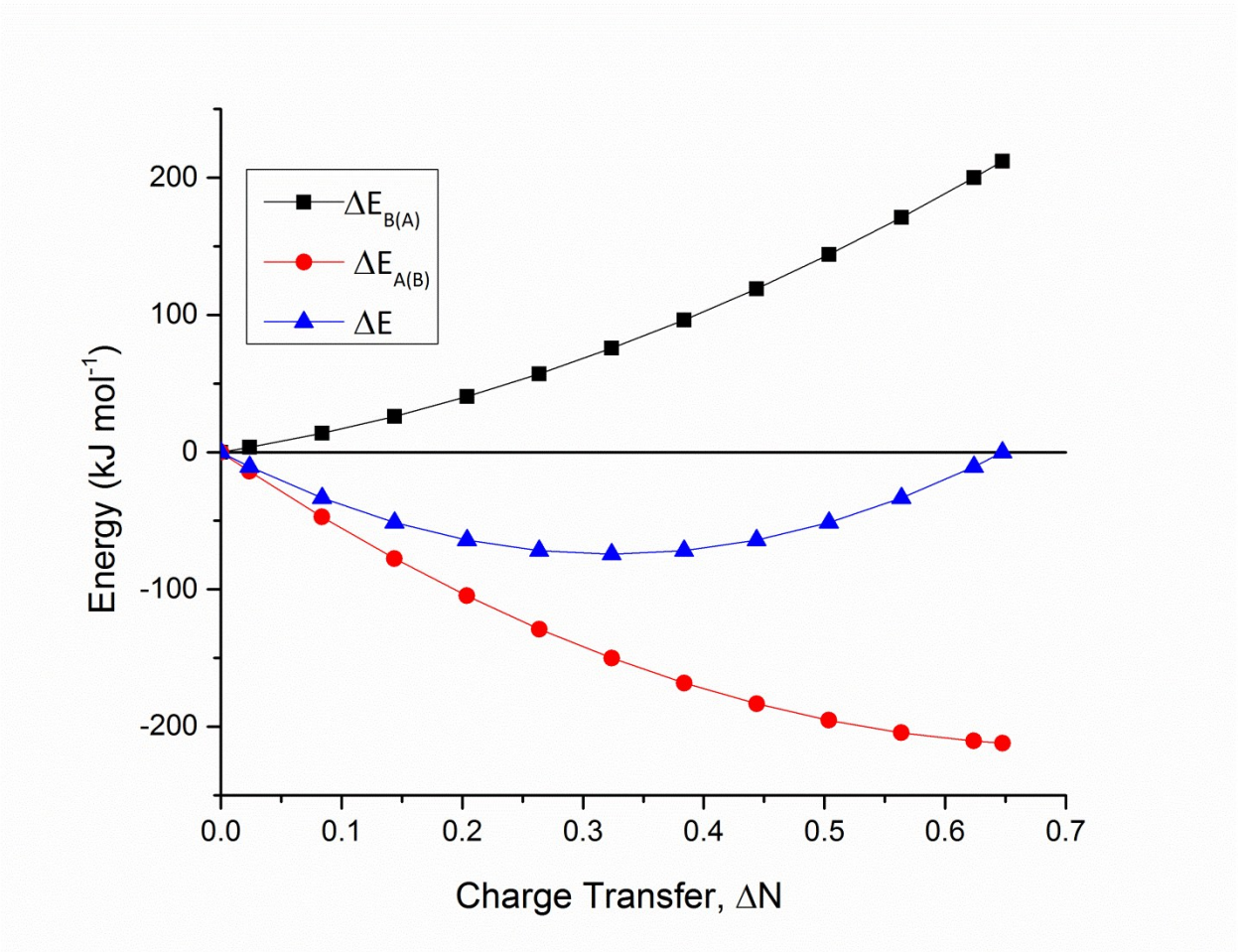


Figure S10. Plot showing the profiles of $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and ΔE with respect to ΔN for dimethylamine (B) and trifluoroborane (A).

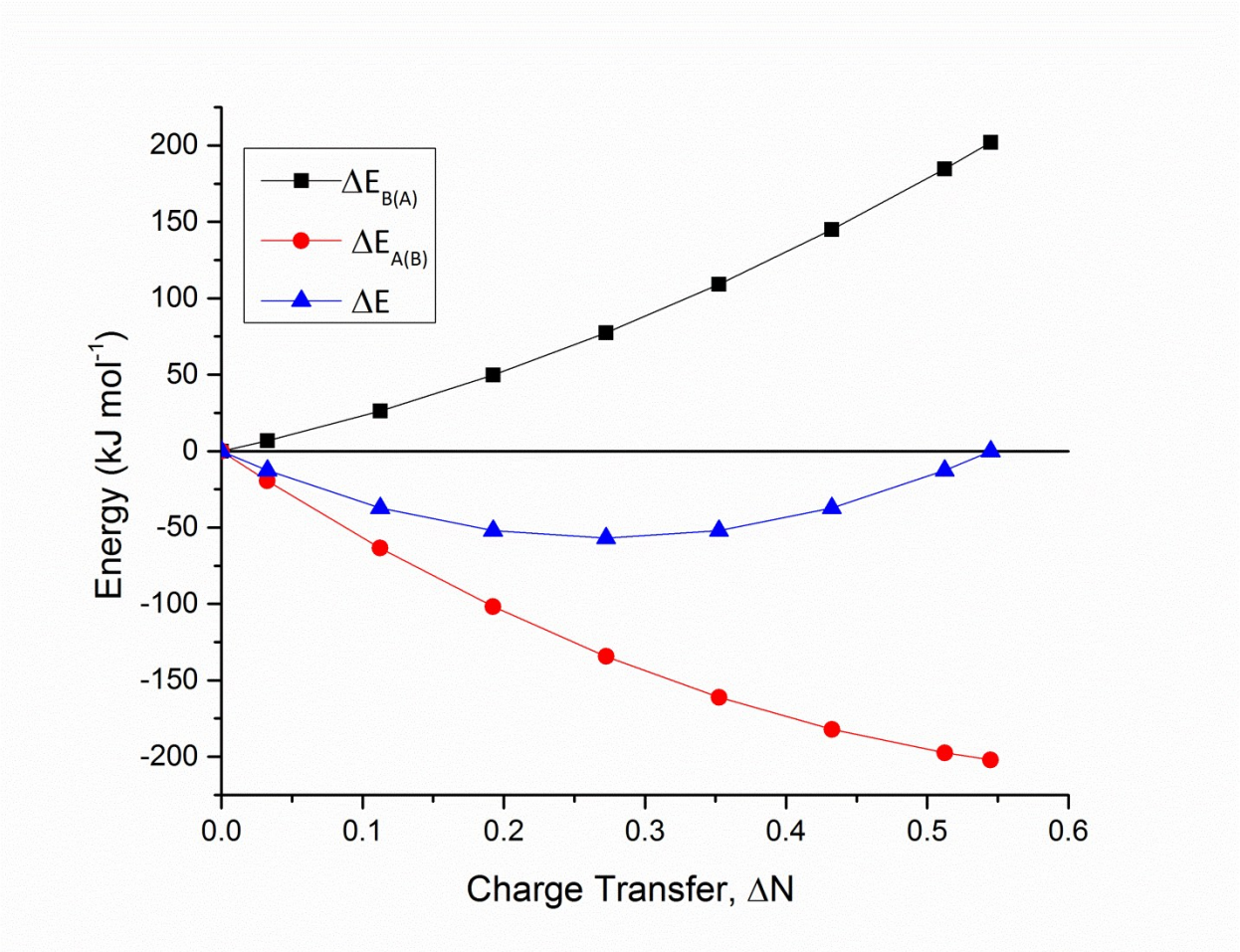


Figure S11. Plot showing the profiles of $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and ΔE with respect to ΔN for trimethylamine (B) and trifluoroborane (A).