Supplementary Information for: Elucidating conformational preference of substituted azobenzenes with intramolecular symmetry-adapted perturbation theory[†]

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[†]Dedicated to the memory of Professor Bogumił Jeziorski.

Table S1: The DLPNO-CCSD(T) total energies (in hartree) for the cis and trans structures of substituted azobenzenes, and the DLPNO-CCSD(T) (cis−trans) conformational energy differences ΔE (in kcal/mol). The results are presented in two basis sets, aDZ and aTZ. For *i*PrAB*t*Bu and *t*BuAB*t*Bu, the aTZ results are estimated according to Eq. (1) in the main text.

	aDZ			aTZ		
	E_{cis}	E_{trans}	ΔE	E_{cis}	E_{trans}	ΔE
System	[hartree]	[hartree]	[kcal/mol]	[hartree]	[hartree]	[kcal/mol]
AB	-571.2441	-571.2601	10.020	-571.7273	-571.7455	11.422
ABMe	-649.6641	-649.6794	9.607	-650.2202	-650.2379	11.124
MeABMe	-728.0841	-728.0986	9.087	-728.7129	-728.7302	10.819
ABEt	-728.0797	-728.0928	8.216	-728.7077	-728.7239	10.155
MeABEt	-806.5007	-806.5121	7.120	-807.2011	-807.2162	9.510
EtABEt	-884.9149	-884.9255	6.623	-885.6876	-885.7022	9.177
AB*i*Pr	-806.4976	-806.5103	8.003	-807.1970	-807.2129	9.973
MeAB*i*Pr	-884.9186	-884.9295	6.851	-885.6903	-885.7052	9.350
EtAB*i*Pr	-963.3327	-963.3430	6.480	-964.1768	-964.1912	9.026
*i*PrAB*i*Pr	-1041.7537	-1041.7603	4.099	-1042.6682	-1042.6800	7.398
AB*t*Bu	-884.9161	-884.9287	7.952	-885.6860	-885.7019	9.992
MeAB*t*Bu	-963.3379	-963.3476	6.115	-964.1796	-964.1939	8.970
EtAB*t*Bu	-1041.7521	-1041.7614	5.837	-1042.6661	-1042.6802	8.811
*i*PrAB*t*Bu	-1120.1736	-1120.1786	3.164	-1121.1660	-1121.1765	6.565
*t*BuAB*t*Bu	-1198.5937	-1198.5974	2.305	-1199.6573	-1199.6671	6.198

Table S2: ISAPT(SIAO1)/aTZ interaction energy contributions for the cis structures of substituted azobenzenes, in kcal/mol.

System	Electrostatics	Exchange	Induction	Dispersion	Total ISAPT
AB	-5.979	11.493	-2.058	-7.575	-4.119
ABMe	-6.076	11.980	-2.112	-8.021	-4.230
MeABMe	-6.644	12.863	-2.338	-8.756	-4.875
ABEt	-7.224	13.868	-2.417	-9.707	-5.480
MeABEt	-8.101	16.121	-2.599	-11.441	-6.020
EtABEt	-8.050	16.263	-2.629	-11.809	-6.225
AB*i*Pr	-7.270	14.153	-2.445	-10.151	-5.713
MeAB*i*Pr	-8.071	16.307	-2.622	-11.945	-6.331
EtAB*i*Pr	-8.174	16.611	-2.658	-12.280	-6.501
*i*PrAB*i*Pr	-8.548	19.270	-2.823	-16.153	-8.254
AB*t*Bu	-7.494	14.407	-2.491	-10.119	-5.696
MeAB*t*Bu	-8.868	18.075	-2.765	-12.965	-6.523
EtAB*t*Bu	-9.028	18.484	-2.825	-13.426	-6.794
*i*PrAB*t*Bu	-8.922	20.666	-2.924	-17.689	-8.868
*t*BuAB*t*Bu	-9.751	22.284	-3.119	-18.750	-9.336

Table S3: ISAPT(SIAO1)/aTZ interaction energy contributions for the trans structures of substituted azobenzenes, in kcal/mol.

System	Electrostatics	Exchange	Induction	Dispersion	Total ISAPT
AB	-2.685	-0.217	-1.581	-1.570	-6.054
ABMe	-3.552	0.615	-2.050	-1.963	-6.950
MeABMe	-4.794	1.671	-2.411	-2.209	-7.743
ABEt	-3.554	0.622	-2.051	-1.991	-6.975
MeABEt	-4.794	1.680	-2.408	-2.243	-7.765
EtABEt	-4.800	1.691	-2.409	-2.281	-7.798
AB*i*Pr	-3.534	0.619	-2.041	-2.049	-7.005
MeAB*i*Pr	-4.763	1.675	-2.396	-2.312	-7.796
EtAB*i*Pr	-4.763	1.684	-2.393	-2.354	-7.825
*i*PrAB*i*Pr	-4.787	1.701	-2.410	-2.383	-7.879
AB*t*Bu	-3.601	0.642	-2.089	-2.091	-7.139
MeAB*t*Bu	-4.796	1.710	-2.411	-2.348	-7.844
EtAB*t*Bu	-4.814	1.732	-2.429	-2.406	-7.917
*i*PrAB*t*Bu	-4.843	1.752	-2.449	-2.437	-7.978
*t*BuAB*t*Bu	-4.730	1.700	-2.386	-2.538	-7.955

Table S4: ISAPT(C)/aTZ interaction energy contributions for the cis structures of substituted azobenzenes, in kcal/mol.

System	Electrostatics	Exchange	Induction	Dispersion	Total ISAPT
AB	-1.727	16.630	-3.043	-7.801	4.058
ABMe	-2.230	17.578	-3.115	-8.276	3.956
MeABMe	-3.645	19.536	-3.399	-9.046	3.447
ABEt	-4.196	20.771	-3.520	-10.021	3.035
MeABEt	-5.907	23.907	-3.761	-11.811	2.429
EtABEt	-5.824	24.248	-3.812	-12.193	2.418
AB*i*Pr	-4.237	21.067	-3.564	-10.467	2.799
MeAB*i*Pr	-5.765	23.984	-3.797	-12.313	2.108
EtAB*i*Pr	-5.930	24.444	-3.854	-12.658	2.003
*i*PrAB*i*Pr	-6.658	28.596	-4.014	-16.631	1.294
AB*t*Bu	-4.729	21.493	-3.611	-10.441	2.712
MeAB*t*Bu	-7.358	26.814	-3.991	-13.392	2.073
EtAB*t*Bu	-7.552	27.305	-4.074	-13.860	1.818
*i*PrAB*t*Bu	-7.619	31.203	-4.118	-18.230	1.236
*t*BuAB*t*Bu	-8.337	32.018	-4.374	-19.256	0.051

Table S5: ISAPT(C)/aTZ interaction energy contributions for the trans structures of substituted azobenzenes, in kcal/mol.

System	Electrostatics	Exchange	Induction	Dispersion	Total ISAPT
AB	0.841	0.638	-1.924	-1.466	-1.911
ABMe	-0.808	1.522	-2.443	-1.816	-3.545
MeABMe	-2.310	2.566	-2.855	-2.037	-4.636
ABEt	-0.830	1.528	-2.446	-1.843	-3.591
MeABEt	-2.332	2.574	-2.852	-2.070	-4.680
EtABEt	-2.361	2.586	-2.852	-2.107	-4.735
AB*i*Pr	-0.794	1.528	-2.438	-1.901	-3.605
MeAB*i*Pr	-2.295	2.574	-2.840	-2.139	-4.701
EtAB*i*Pr	-2.317	2.582	-2.837	-2.180	-4.752
*i*PrAB*i*Pr	-2.374	2.600	-2.853	-2.207	-4.835
AB*t*Bu	-0.937	1.559	-2.489	-1.939	-3.806
MeAB*t*Bu	-2.424	2.614	-2.847	-2.173	-4.829
EtAB*t*Bu	-2.468	2.637	-2.866	-2.228	-4.925
*i*PrAB*t*Bu	-2.529	2.658	-2.886	-2.257	-5.014
*t*BuAB*t*Bu	-2.389	2.614	-2.821	-2.359	-4.955

Table S6: The (cis−trans) conformational energy differences for substituted azobenzenes, in kcal/mol. The reference value, coming from the DLPNO-CCSD(T)/aTZ calculation, is compared to the sum of the ISAPT(SIAO1)/aTZ noncovalent interaction energy difference plus the deformation effect as estimated by intermediate systems according to either Eq. (5) or (6). The data in this table form the basis for the scatter plots in Figs. 10 and 11 in the main text.

		Interaction	Deformation		Interaction+deformation	
System	Reference	ISAPT	Eq. (5)	Eq. (6)	Eq. (5)	Eq. (6)
AB	11.422	1.935	7.321	12.124	9.256	14.060
ABMe	11.124	2.720	7.173	11.856	9.892	14.576
MeABMe	10.819	2.867	7.044	11.702	9.911	14.569
ABEt	10.155	1.495	6.766	11.653	8.261	13.147
MeABEt	9.510	1.745	6.629	11.445	8.374	13.190
EtABEt	9.177	1.573	6.459	11.382	8.032	12.955
AB*i*Pr	9.973	1.293	6.785	11.590	8.077	12.883
MeAB*i*Pr	9.350	1.465	6.678	11.478	8.143	12.943
EtAB*i*Pr	9.026	1.324	6.598	11.433	7.922	12.757
*i*PrAB*i*Pr	7.398	-0.375	5.899	11.741	5.524	11.366
AB*t*Bu	9.992	1.443	6.766	11.594	8.209	13.037
MeAB*t*Bu	8.970	1.321	6.317	11.351	7.638	12.672
EtAB*t*Bu	8.811	1.123	6.376	11.511	7.499	12.633
*i*PrAB*t*Bu	6.565	-0.891	5.298	12.083	4.407	11.193
*t*BuAB*t*Bu	6.198	-1.381	5.911	11.944	4.530	10.562

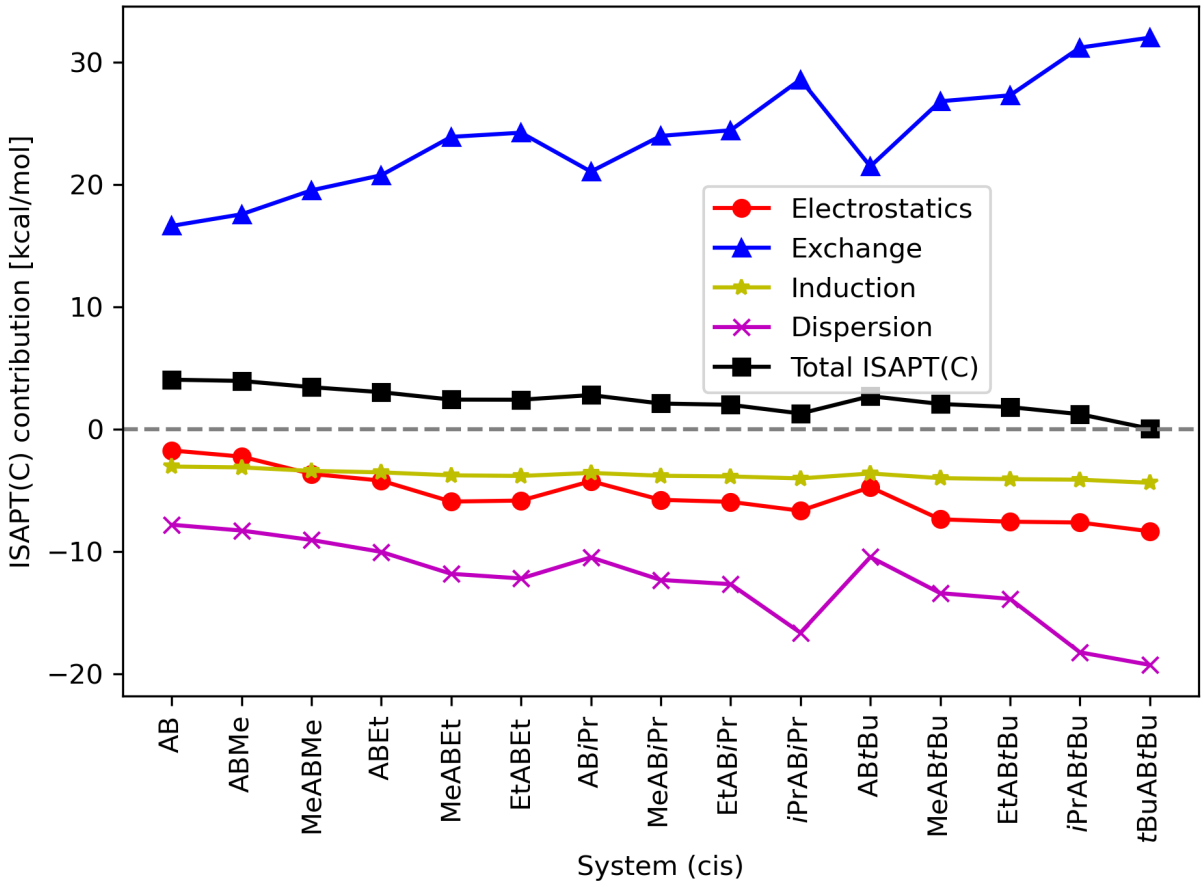


Figure S1: ISAPT(C)/aTZ intramolecular nonbonded energy contributions for the cis isomers of substituted azobenzenes.

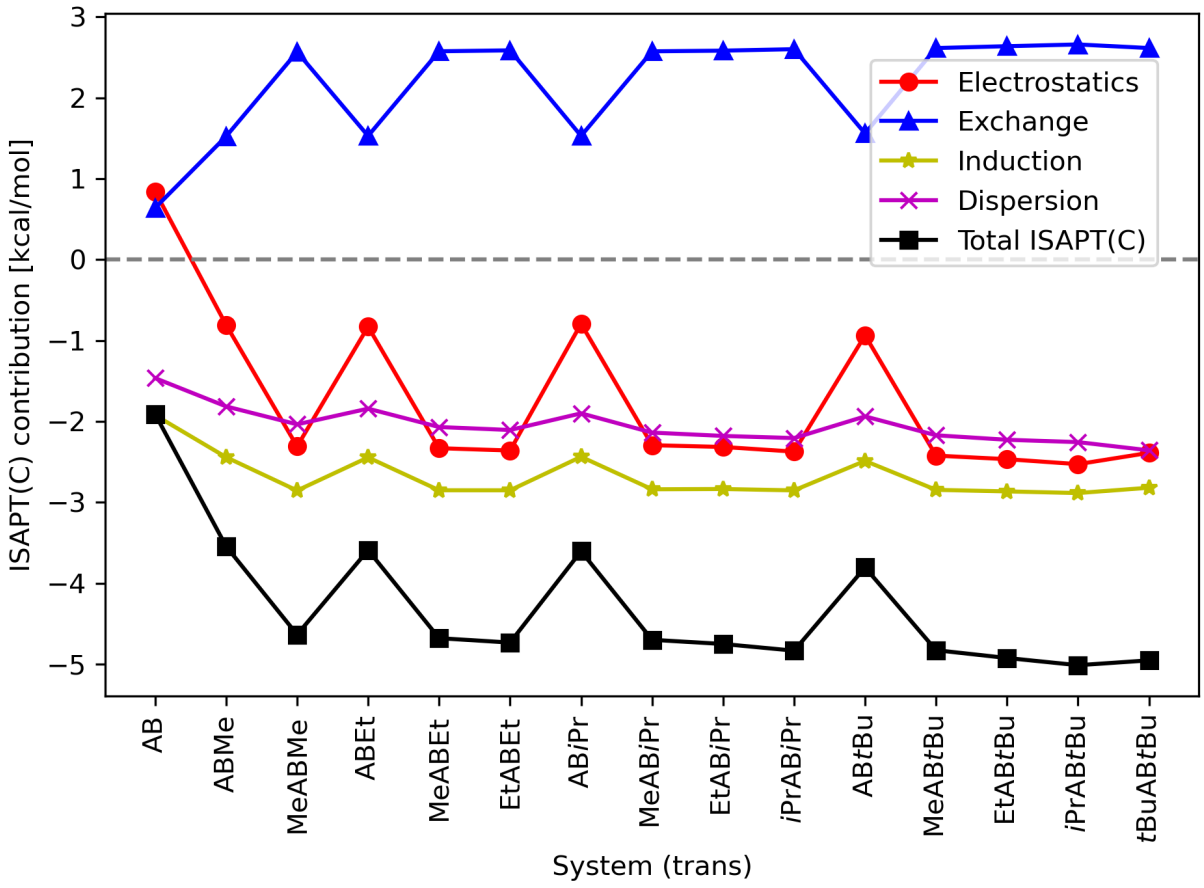


Figure S2: ISAPT(C)/aTZ intramolecular nonbonded energy contributions for the trans isomers of substituted azobenzenes.

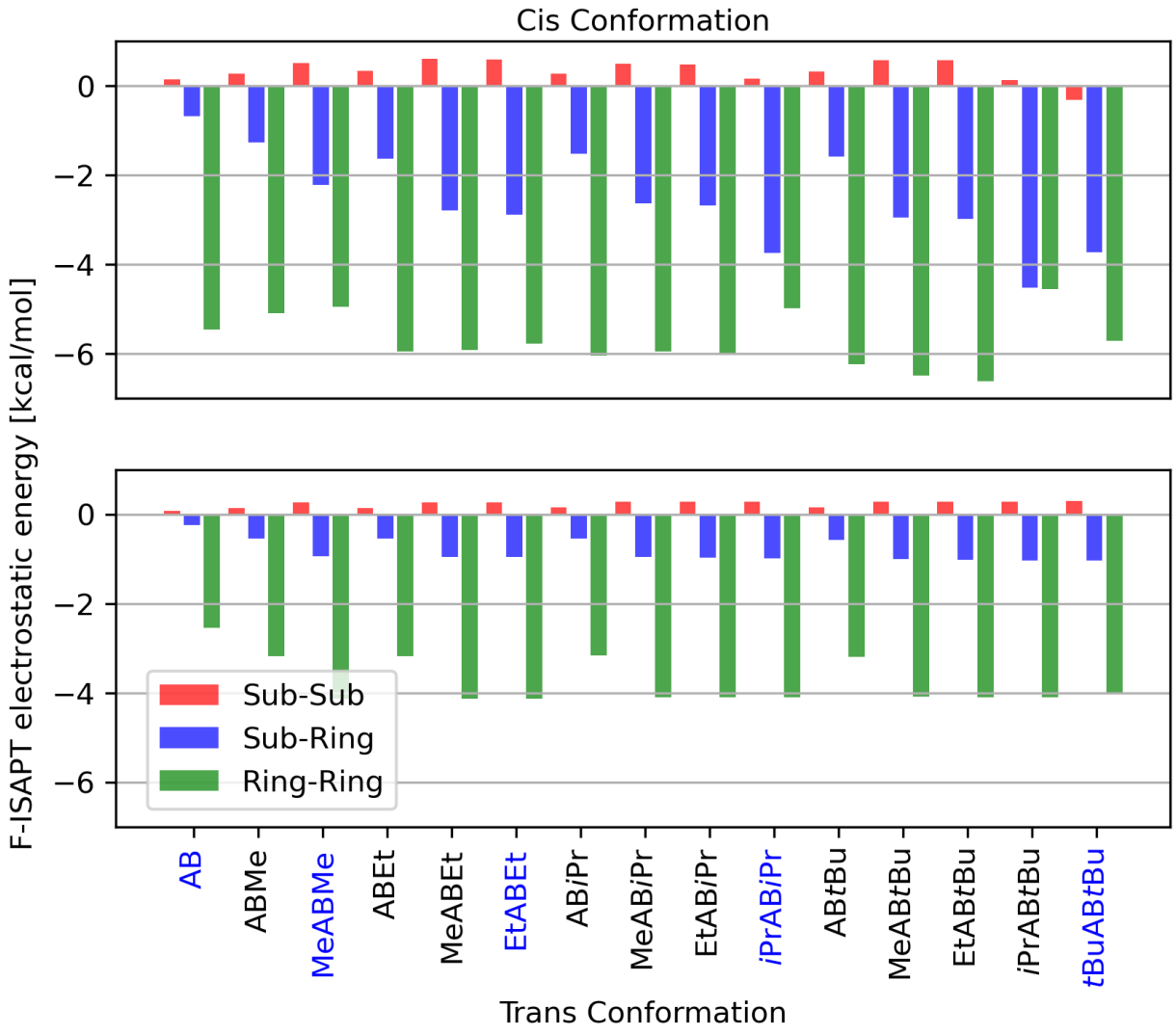


Figure S3: F-ISAPT(SIAO1)/aTZ intramolecular electrostatic energy decomposition into substituent-substituent, ring-ring, and mixed substituent-ring contributions. The substituents are all in the meta positions and, in some systems, might amount to only a hydrogen atom.

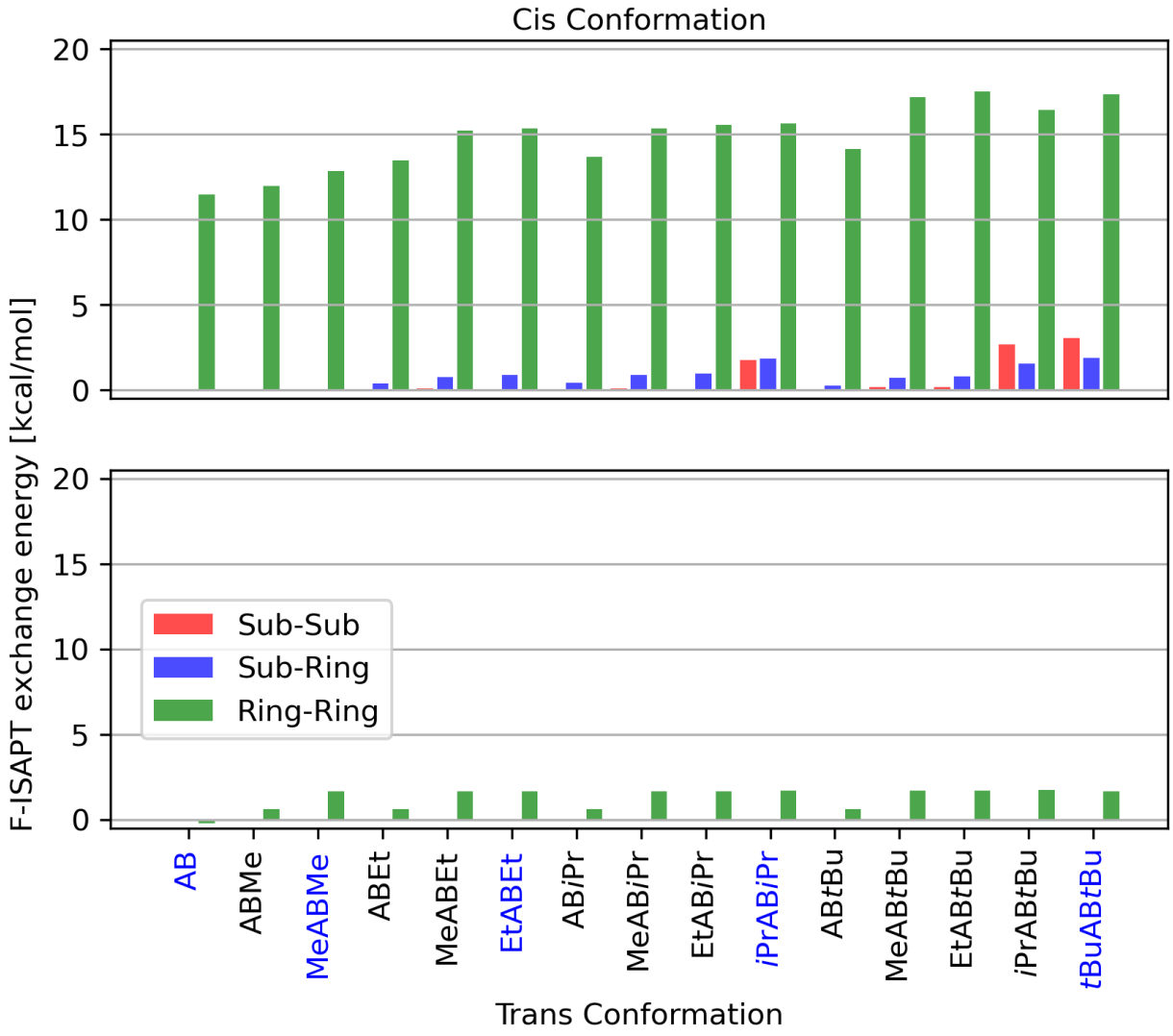


Figure S4: F-ISAPT(SIAO1)/aTZ intramolecular exchange energy decomposition into substituent-substituent, ring-ring, and mixed substituent-ring contributions. The substituents are all in the meta positions and, in some systems, might amount to only a hydrogen atom.

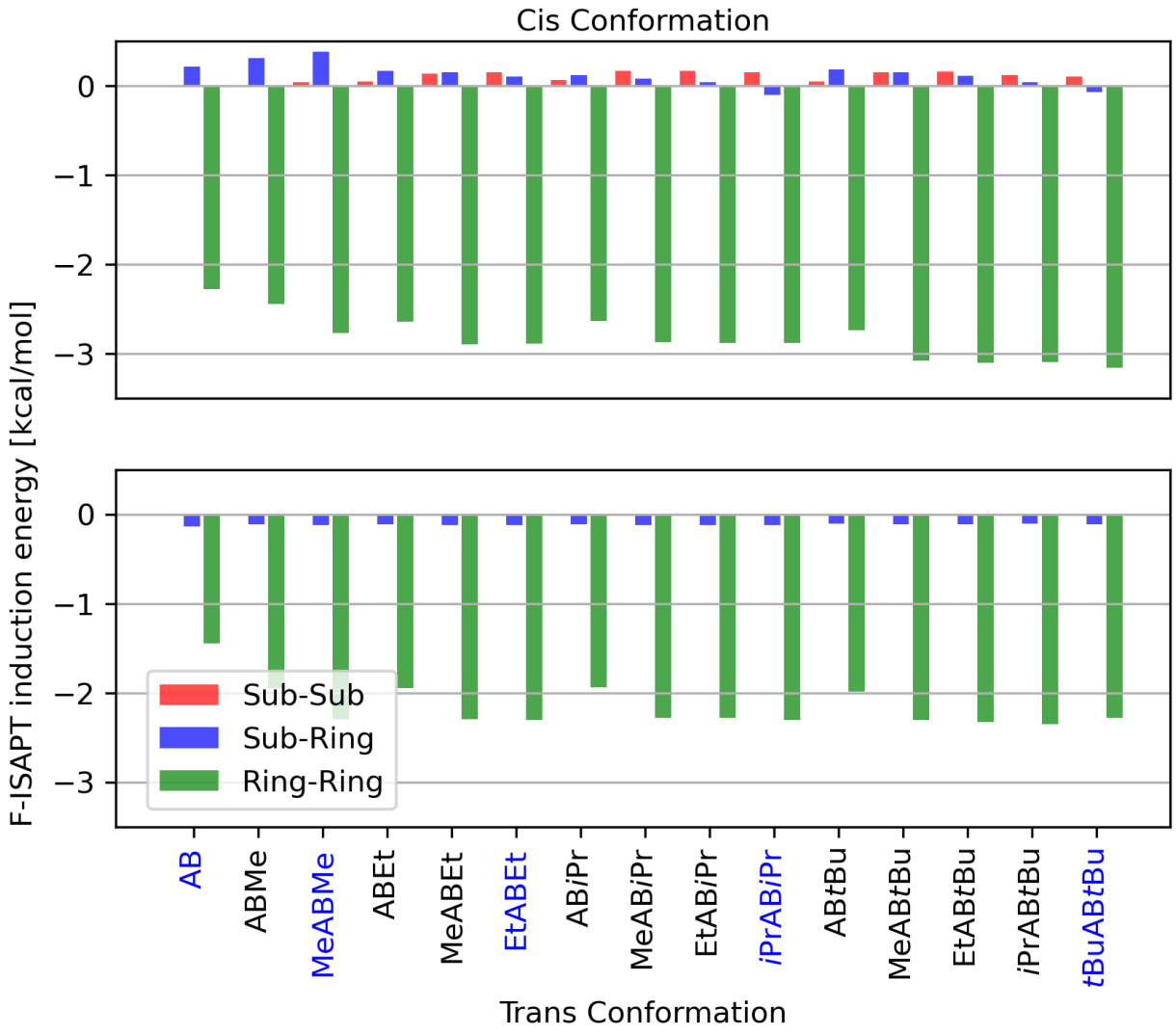


Figure S5: F-ISAPT(SIAO1)/aTZ intramolecular induction energy decomposition into substituent-substituent, ring-ring, and mixed substituent-ring contributions. The substituents are all in the meta positions and, in some systems, might amount to only a hydrogen atom.

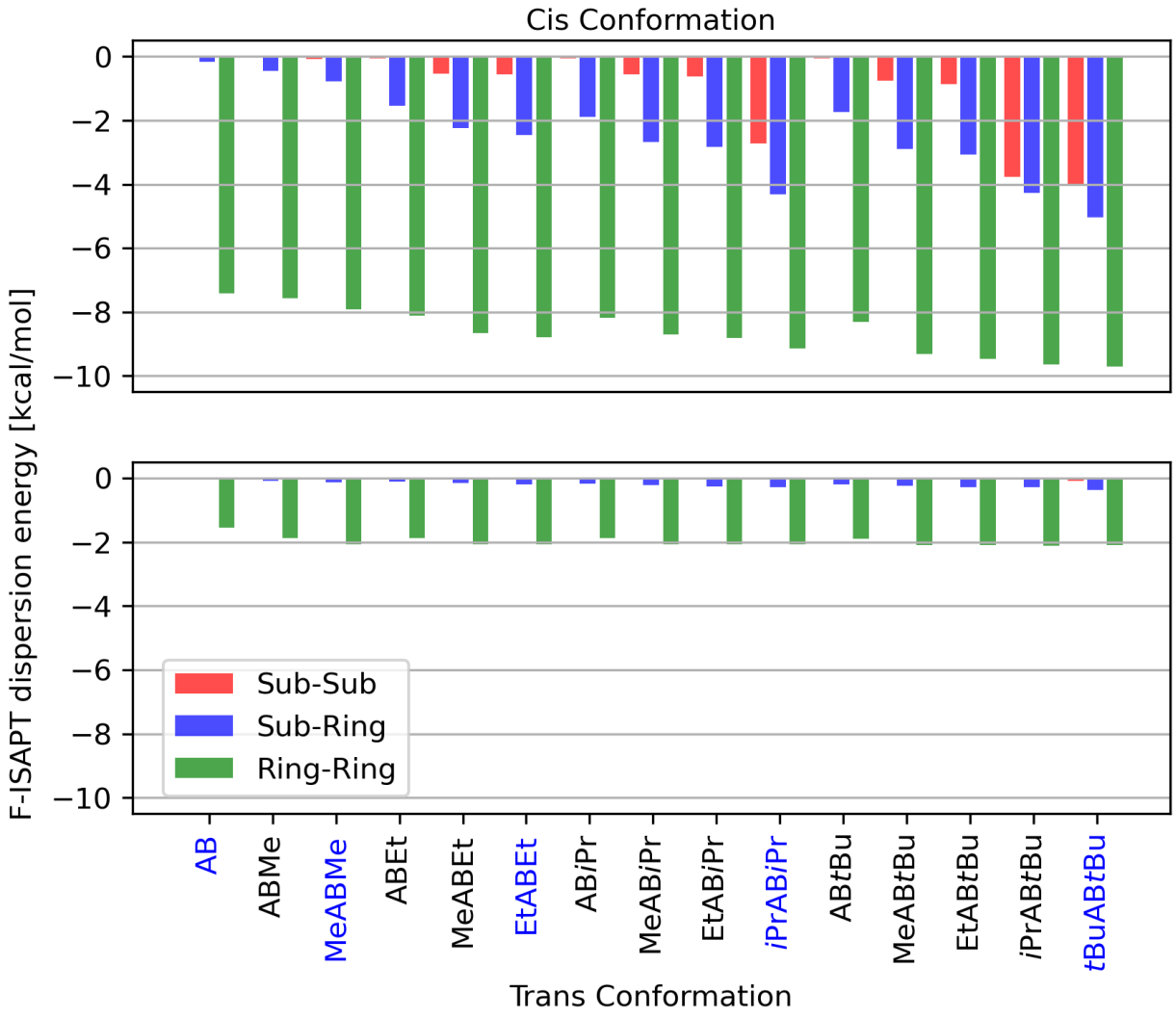


Figure S6: F-ISAPT(SIAO1)/aTZ intramolecular dispersion energy decomposition into substituent-substituent, ring-ring, and mixed substituent-ring contributions. The substituents are all in the meta positions and, in some systems, might amount to only a hydrogen atom.