

Supplementary Materials

**Push-Pull Effect on the Gas-Phase Basicity of Nitriles.
Transmission of the Resonance Effect by
Methylenecyclopropene and Cyclopropenimine π -Systems
Substituted by Two Identical Strong Electron-Donors**

Ewa D. Raczyńska,^{*a} Jean-François Gal,^{*b} Pierre-Charles Maria,^b Hamid Saeidian^{*c}

^a Department of Chemistry, Warsaw University of Life Sciences (SGGW),
ul. Nowoursynowska 159c, 02-776 Warszawa, Poland, E-mail:
ewa_raczynska@sggw.edu.pl

^b Institut de Chimie de Nice, UMR 7272, Université Côte d'Azur, Parc Valrose,
06108 NICE, France, E-mail: Jean-Francois.GAL@univ-cotedazur.fr

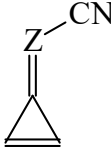
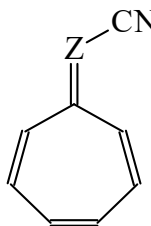
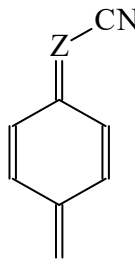
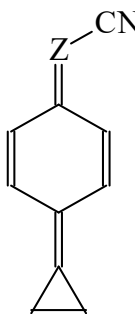
^c Department of Science, Payame Noor University (PNU), P.O. Box: 19395-4697,
Teheran, Iran, E-mail: saeidian1980@gmail.com

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Nomenclature of simple nitriles

Simple nitriles **1-6**, considered in this work, can be named according to the IUPAC names.^{S1} Their nomenclature is given in Table S1.

Table S1. The structures and IUPAC names of simple nitriles considered in this work.

Structure	No	Z	IUPAC name
$\text{H}_2\text{C}=\text{Z}-\text{CN}$	1	CH N	prop-2-enenitrile methylidenecyanamide
$\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{Z}-\text{CN}$	2	CH N	penta-2,4-dienenitrile prop-2-en-1-ylidenecyanamide
	3	CH N	(cycloprop-2-en-1-ylidene)acetone nitrile (cycloprop-2-en-1-ylidene)cyanamide
	4	CH N	(cyclohepta-2,4,6-trien-1-ylidene)acetone nitrile (cyclohepta-2,4,6-trien-1-ylidene)cyanamide
	5	CH N	(4-methylidenecyclohexa-2,5-dien-1-ylidene)acetone nitrile (4-methylidenecyclohexa-2,5-dien-1-ylidene)cyanamide
	6	CH N	[4-(cycloprop-2-en-1-ylidene)cyclohexa-2,5-dien-1-ylidene]acetone nitrile [4-(cycloprop-2-en-1-ylidene)cyclohexa-2,5-dien-1-ylidene]cyanamide

Computational details

For all investigated nitriles, **I.1-I.12** and **II.1-II.12**, geometries of neutral and protonated (cyano and imino) isomers were optimized without restriction in their ground states. Geometrical (bond lengths) and thermochemical (E , H , S , and G) parameters were calculated for real structures possessing all positive frequencies. For selected structures, calculations were performed at the DFT1 {B3LYP/6-311+G(d,p)}, DFT2 {B3LYP/6-311++G(d,p)}, G2, and G2MP2 levels using the Gaussian 03 program,^{S2} and for the other ones at the DFT2 level employing the Gaussian 16.^{S3}

When gas-phase acid-base properties are investigated by quantum-chemical methods for polyfunctional compounds, all principal isomeric phenomena (constitutional, rotational and geometrical isomerism, prototropic tautomerism, intramolecular proton-transfer, etc.) should be considered to avoid various discrepancies linked with the protonation or deprotonation equilibria $B + H^+ = BH^+$. Otherwise, the calculated energetic parameters for this reaction (referred to as PAs/GBs) may correspond to unlikely neutral and protonated or deprotonated forms, such as unfavored neutral and favored ionic isomers, favored neutral and rare ionic isomers, or rare neutral and rare ionic isomers. They may also describe equilibria for completely different constitutional neutral and ionic isomers, rare tautomers, or rare protonation-deprotonation sites. Such kind of treatment of new organic molecules seems to be incomplete, or in some cases even erroneous. It gives scanty information on acid-base properties of new molecules, particularly superacids and superbases that attract great attention of many chemists. Hence, all isomeric phenomena and all reasonable protonation sites have been considered to estimate appropriate PAs/GBs. We started our analyses from the simplest molecules (**I.2** and **II.2**), and next we extensively investigated isomeric phenomena in disubstituted **CPC** and **CPN** derivatives containing push-pull large substituents (**I.10-I.12** and **II.10-II.12**). The structures of all studied isomers for the neutral and monoprotated forms and their relative Gibbs energies are given in Charts S1-S5. Selected thermochemical data for nitriles **I.1-I.12** and **II.1-II.12** are included in Tables S2-S3.

In the HOMA procedure (eq. 3), the DFT2-calculated bond lengths (R_x) for studied fragments were obtained from the optimized geometries of nitriles by applying the GaussView 5.0.8 program. Analogously, the final Cartesian coordinates of the DFT1-optimized structures were taken from the Gaussian 03 out file. The bond lengths (R_x), used in the HOMED estimation, were found by employing the Molden program. Parameters applied in the HOMED procedure (R_0 and α) are summarized in Table S4. The isotropic (-NICS) values were extracted from the Gaussian NMR out file in the following way. After placing the bq(0) and bq(1) above the studied ring in the optimized geometry using the GaussView 5.0.8 software, NMR calculations were performed applying the gauge-independent atomic orbital (GIAO) method^{S4} and the Gaussian 16 software.

When polyfunctional compound exhibits isomerism, quantum-chemical methods give the possibility to estimate gas-phase acidity/basicity parameters for each potential site of protonation/deprotonation in all considered isomers. According to the Brønsted theory, PA and GB calculated for individual isomer B_i correspond to the following equilibrium: $B_iH^+ \rightarrow B_i + H^+$, and measure gas-phase basicity of selected site in B_i . For simple derivatives that do not display significant isomeric variations, we estimated the PAs and GBs according to equations (1) and (2), respectively, for the cyano N atom and additionally for the imino N(Z) atom in compounds of series **II**. For diguanidino and diphosphazeno derivatives, the PAs and GBs were also estimated for the imino N(X) atom in substituent X. The PAs and GBs calculated for isomers of **I.1-I.12** and **II.1-II.12** are summarized in Table S5.

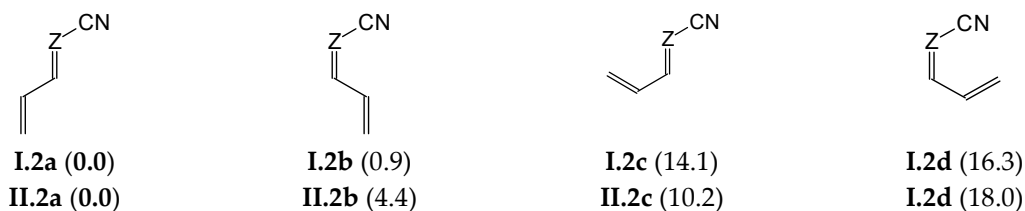


Chart S1. The four isomers (a-d) possible for neutral **I.2** (Z: CH) and **II.2** (Z: N) and their relative Gibbs energies (given in parenthesis in kJ mol⁻¹ at 298K) estimated at the DFT1 level.

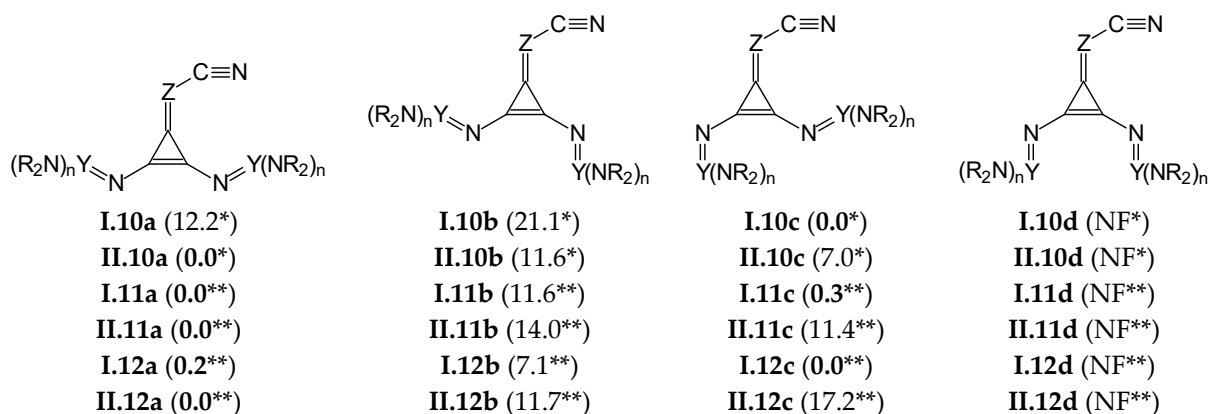


Chart S2. The four isomers considered in this work for neutral **CPC** and **CPN** derivatives (**I.10-I.12** and **II.10-II.12**) containing two guanidino (Y: C, n = 2) or phosphazeno (Y: P, n = 3) groups and their relative Gibbs energies (given in parenthesis in kJ mol⁻¹ at 298K) estimated at the DFT1 (*) or DFT2 (**) levels (NF – structure not found).

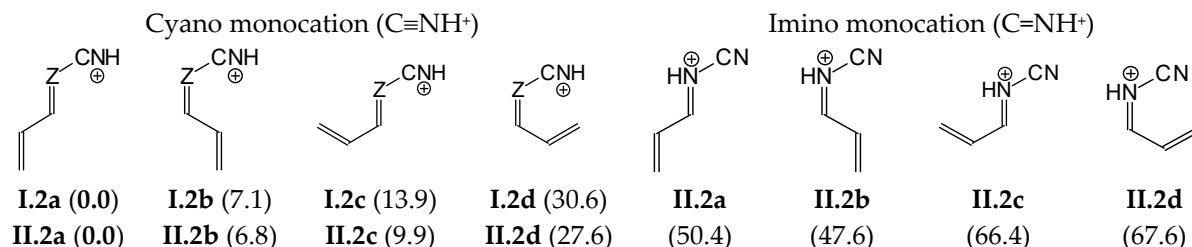


Chart S3. Relative Gibbs energies (given in parenthesis in kJ mol⁻¹ at 298K) for four isomers (a-b) possible for monoprotonated forms of **I.2** (Z: CH) and **II.2** (Z: N) estimated at the DFT1 level.

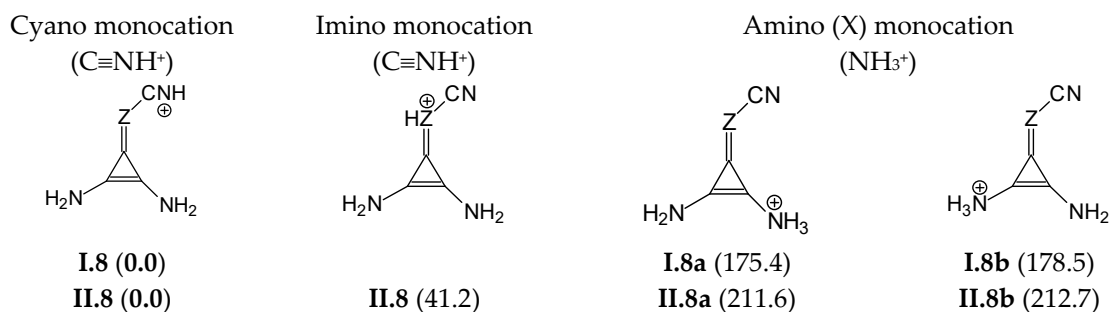


Chart S4. Relative Gibbs energies (given in parenthesis in kJ mol⁻¹ at 298K) for monoprotonated forms of **I.8** (Z: CH) and **II.8** (Z: N) estimated at the DFT1 level.

Cyano monocation ($C\equiv NH^+$)

I.10a (24.1*)	I.10b (0.0*)	I.10c (3.3*)	I.10d (20.0*)
II.10a (23.3*)	II.10b (0.0*)	II.10c (15.3*)	II.10d (35.8*)
I.11a (10.6**)	I.11b (0.0**)	I.11c (1.5**)	I.11d (19.0**)
II.11a (7.8**)	II.11b (0.0**)	II.11c (8.4**)	II.11d (NF**)
I.12a (21.5**)	I.12b (9.6**)	I.12c (19.1**)	I.12d (0.0**)
II.12a (9.4**)	II.12b (0.0**)	II.12c (NF**)	II.12d (37.7**)

Imino (X_{syn}) monocation ($C=NH^+$)

I.10a (30.2*)	I.10b (38.3*)	I.10c (51.6*)	I.10d (82.1*)
II.10a (50.5*)	II.10b (68.4*)	II.10c (91.8*)	II.10d (134.5*)
I.11a (4.8**)	I.11b (14.5**)	I.11c (22.1**)	I.11d (NF**)
II.11a (29.3**)	II.11b (45.1**)	II.11c (58.1**)	II.11d (NF**)
I.12a (33.3**)	I.12b (28.4**)	I.12c (49.5**)	I.12d (NF**)
II.12a (46.9**)	II.12b (51.8**)	II.12c (78.2**)	II.12d (NF**)

Imino (X_{anti}) monocation ($C=NH^+$)

I.10a (45.6*)	I.10b (89.4*)	I.10c (27.0*)	I.10d (NF*)
II.10a (55.3*)	II.10b (97.3*)	II.10c (67.6*)	II.10d (NF*)
I.11a (15.5**)	I.11b (48.0**)	I.11c (17.9**)	I.11d (NF**)
II.11a (33.6**)	II.11b (68.3**)	II.11c (46.0**)	II.11d (NF**)
I.12a (40.9**)	I.12b (68.0**)	I.12c (34.7**)	I.12d (NF**)
II.12a (50.0**)	II.12b (71.7**)	II.12c (57.1**)	II.12d (NF**)

Imino (Z) monocation ($C=NH^+$)

II.10a (52.8*)	II.10b (46.2*)	II.10c (26.0*)	II.10d (57.4*)
II.11a (27.0**)	II.11b (29.4**)	II.11c (15.9**)	II.11d (NF**)
II.12a (35.6**)	II.12b (26.0**)	II.12c (28.8**)	II.12d (NF**)

Chart S5. Isomers considered in this work for monoprotonated derivatives (**I.10-I.12** and **II.10-II.12**) containing two guanidino (Y: C, n = 2) or phosphazeno (Y: P, n = 3) groups and their relative Gibbs energies (given in parenthesis in kJ mol⁻¹ at 298K) estimated at the DFT1 (*) or DFT2 (**) levels (NF – structure not found, NC – structure not calculated).

Table S2. Selected thermochemical data (H and G in Hartree) for simple nitriles (**1-9**) calculated at the DFT1, DFT2, G2, and/or G2MP2 levels for their neutral and cyano and imino N protonated forms:

(a) series I with Z = CH					
Compound	Method	$H(\text{neutral})$	$G(\text{neutral})$	$H(\text{C}\equiv\text{NH}^+)$	$G(\text{C}\equiv\text{NH}^+)$
I.1	DFT1	-170.827190	-170.838155	-171.1266986	-171.158665
	DFT2	-170.827225	-170.858193	-171.127066	-171.158742
	G2	-170.528847	-170.559865	-170.825374	-170.856960
	G2MP2	-170.525059	-170.556077	-170.821822	-170.853409
I.2a	DFT1	-248.219121	-248.255824	-248.534431	-248.572677
	DFT2	-248.219185	-248.255913	-248.534530	-248.572751
	G2	-247.777028	-247.814082	-248.084815	-248.122501
	G2MP2	-247.771792	-247.808846	-248.079665	-248.117351
I.2b	DFT1	-248.218754	-248.255474	-248.531863	-248.569982
	DFT2	-248.218805	-248.255519	-248.531962	-248.570052
	G2	-247.777244	-247.814232	-248.083020	-248.120681
	G2MP2	-247.772062	-247.809050	-248.077915	-248.115575
I.2c	DFT1	-248.213360	-248.250441	-248.527895	-248.567384
I.2d	DFT1	-248.212255	-248.249622	-248.523115	-248.561031
I.3	DFT1	-246.956008	-246.991320	-247.290894	-247.326809
	DFT2	-246.956054	-246.991366	-247.290970	-247.326883
	G2	-246.515270	-246.550649	-246.843366	-246.880856
	G2MP2	-246.510013	-246.545391	-246.838222	-246.875712
I.4	DFT1	-401.820723	-401.863668	-402.164998	-402.208249
	DFT2	-401.820817	-401.863757	-402.165054	-402.208324
I.5	DFT1	-401.831987	-401.874735	-402.166379	-402.209776
	DFT2	-401.832059	-401.874811	-402.166449	-402.209859
I.6	DFT1	-477.959591	-478.006685	-478.327781	-478.375358
	DFT2	-477.959720	-478.006848	-478.327923	-478.375519
I.7	DFT1	-325.572510	-325.616525	-325.922299	-325.967769
	DFT2	-325.572587	-325.616576	-325.922411	-325.967792
I.8	DFT1	-357.693625	-357.735929	-358.061283	-358.103669
	DFT2	-357.693742	-357.736039	-358.061437	-358.103819
I.9	DFT1	-514.841700	-514.898447	-515.219638	-515.279016
	DFT2	-514.841905	-514.898701	-515.219714	-515.279181

(b) series II with Z = N					
Compound	Method	$H(\text{neutral})$	$G(\text{neutral})$	$H(\text{C}\equiv\text{NH}^+)$ [$H(\text{ZH}^+)$]	$G(\text{C}\equiv\text{NH}^+)$ [$G(\text{ZH}^+)$]
II.1	DFT1	-186.872081	-186.902582	-187.173445	-187.205111
				[-187.150911]	[-187.181913]
	DFT2	-186.872119	-186.902620	-187.173500	-187.205166
				[-187.150952]	[-187.181956]
	G2	-186.561322	-186.591846	-186.858070	-186.889289
II.2a				[-186.841941]	[-186.872961]
	G2MP2	-186.557009	-186.587532	-186.854101	-186.885320
				[-186.837911]	[-186.868930]
	DFT1	-264.269863	-264.306112	-264.593034	-264.631001
				[-264.575084]	[-264.611787]
	DFT2	-264.269916	-264.306164	-264.593107	-264.631073

				[-264.575165]	[264.611863]
	G2	-263.814631	-263.851139	-264.128765	-264.166108
				[-264.117783]	[-264.154717]
	G2MP2	-263.808669	-263.845177	-264.122944	-264.160288
				[-264.111901]	[-264.148836]
II.2b	DFT1	-264.268099	-264.304422	-264.590142	-264.628390
				[-264.576194]	[-264.612866]
	DFT2	-264.268160	-264.304482	-264.590228	-264.628484
				[-264.576264]	[-264.612937]
	G2	-263.813798	-263.850303	-264.126640	-264.164070
				[-264.119557]	[-264.156382]
	G2MP2	-263.807874	-263.844379	-264.120897	-264.158327
				[-264.113678]	[-264.150503]
II.2c	DFT1	-264.265505	-264.302220	-264.589110	-264.627214
				[-264.566305]	[-264.605716]
II.2d	DFT1	-264.262868	-264.299253	-264.582374	-264.620470
				[-264.568432]	[-264.605261]
II.3	DFT1	-263.012916	-263.047710	-263.350337	-263.387202
				[-263.331104]	[-263.366444]
	DFT2	-263.012945	-263.047743	-263.350381	-263.387222
				[-263.331172]	[-263.366506]
	G2	-262.559635	-262.594460	-262.890579	-262.926665
				[-262.879128]	[-262.914646]
	G2MP2	-262.553558	-262.588383	-262.884755	-262.920841
				[-262.873237]	[-262.908755]
II.4	DFT1	-417.879911	-417.922383	-418.235320	-418.279203
				[-418.223870]	[-418.266706]
	DFT2	-417.880116	-417.922610	-418.235522	-418.279408
				[-418.223992]	[-418.266846]
II.5	DFT1	-417.885684	-417.928055	-418.233144	-418.277805
				[-418.223339]	[-418.266204]
	DFT2	-417.885808	-417.928191	-418.233298	-418.277969
				[-418.223439]	[-418.266313]
II.6	DFT1	-494.019330	-494.065923	-494.399498	-494.447635
				[-494.392911]	[-494.440129]
	DFT2	-494.019395	-494.066008	-494.399583	-494.447728
				[-494.393007]	[-494.440259]
II.7	DFT1	-341.631452	-341.675186	-341.984488	-342.031421
				[-341.970849]	[-342.016382]
	DFT2	-341.631513	-341.675230	-341.984582	-342.031386
				[-341.970949]	[-342.016365]
II.8	DFT1	-373.757225	-373.799742	-374.126439	-374.168958
				[-374.111096]	[-374.153270]
	DFT2	-373.757327	-373.799849	-374.126554	-374.169070
				[-374.111231]	[-374.153413]
II.9	DFT1	-530.906978	-530.963795	-531.287205	-531.346306
				[-531.273062]	[-531.332109]
	DFT2	-530.907113	-530.963805	-531.287405	-531.346555
				[-531.273282]	[-531.332533]

Table S3. Selected thermochemical data (H and G in Hartree) for cycloprop-2-en-1-ylidene derivatives of acetonitrile (**I.10-I.12**) cyanamide (**II.10-II.12**) with two large substituents calculated at the DFT1 or DFT2 level for their neutral, cyano, and imino N (Z , X_{syn} , and X_{anti}) protonated forms.

Compound	Method	$H(\text{neutral})$ $G(\text{neutral})$	$H(\text{C}\equiv\text{NH}^+)$ $G(\text{C}\equiv\text{NH}^+)$	$H(\text{ZH}^+)$ $G(\text{ZH}^+)$	$H(X_{\text{syn}}\text{H}^+)$ $G(X_{\text{syn}}\text{H}^+)$	$H(X_{\text{anti}}\text{H}^+)$ $G(X_{\text{anti}}\text{H}^+)$
I.10a	DFT1	-655.355945	-655.728858	-	-655.727403	-655.721555
		-655.413245	-655.788816		-655.786470	-655.780619
I.10b	DFT1	-655.352295	-655.738191	-	-655.722773	-655.704598
		-655.409862	-655.797981		-655.783394	-655.763926
I.10c	DFT1	-655.361188	-655.737068	-	-655.719616	-655.728396
		-655.417898	-655.796735		-655.778314	-655.787684
I.10d	DFT1	Not found	-655.730102	-	-655.708945	Not found
		(go to I.10c)	-655.790568		-655.766692	(go to I.10c)
II.10a	DFT1	-671.427405	-671.800748	-671.790152	-671.792168	-671.790676
		-671.483992	-671.860934	-671.849675	-671.850572	-671.848730
II.10b	DFT1	-671.422738	-671.810282	-671.793085	-671.784715	-671.774313
		-671.479574	-671.869803	-671.852192	-671.843766	-671.832751
II.10c	DFT1	-671.425208	-671.803408	-671.800980	-671.776662	-671.787492
		-671.481323	-671.863990	-671.859888	-671.834819	-671.845213
II.10d	DFT1	Not found	-671.795555	-671.787984	-671.761074	Not found
		(go to II.10c)	-671.856181	-671.847932	-671.818583	(go to II.10c)
I.11a	DFT2	-969.617721	-970.005058	-	-970.009357	-970.004272
		-969.701982	-970.090719		-970.092939	-970.088082
I.11b	DFT2	-969.611949	-970.009607	-	-970.004267	-969.990496
		-969.697565	-970.094753		-970.089223	-970.076450
I.11c	DFT2	-969.617762	-970.009821	-	-970.001757	-970.004302
		-969.701862	-970.094180		-970.086340	-970.087922
I.11d	DFT2	Not found	-970.000489	-	Not found	Not found
			-970.087512			
II.11a	DFT2	-985.684640	-986.075929	-986.069701	-986.071391	-986.069339
		-985.768210	-986.162094	-986.154794	-986.153923	-986.152260
II.11b	DFT2	-985.677935	-986.079819	-986.068583	-986.063936	-986.053912
		-985.762862	-986.165080	-986.153855	-986.147904	-986.139073
II.11c	DFT2	-985.680505	-986.076854	-986.074684	-986.059250	-986.064861
		-985.763855	-986.161875	-986.159012	-986.142934	-986.147574
II.11d	DFT2	Not found	Not found	Not found	Not found	Not found
I.12a	DFT2	-1845.233382	-1845.637109	-	-1845.634908	-1845.633388
		-1845.345316	-1845.750630		-1845.746131	-1845.743233
I.12b	DFT2	-1845.230255	-1845.642336	-	-1845.633537	-1845.620084
		-1845.342696	-1845.755167		-1845.748029	-1845.732928
I.12c	DFT2	-1845.233872	-1845.639229	-	-1845.628697	-1845.633858
		-1845.345395	-1845.751551		-1845.739963	-1845.745613
I.12d	DFT2	Not found	-1845.645442	-	Not found	Not found
			-1845.758830			
II.12a	DFT2	-1861.307573	-1861.712715	-1861.705910	-1861.701562	-1861.700179
		-1861.418174	-1861.825479	-1861.817036	-1861.811203	-1861.810006
II.12b	DFT2	-1861.302911	-1861.716282	-1861.706907	-1861.697181	-1861.689097
		-1861.413725	-1861.829054	-1861.819151	-1861.809338	-1861.801737
II.12c	DFT2	-1861.300972	Not found	-1861.707141	-1861.688641	-1861.695800
		-1861.411608		-1861.818373	-1861.799286	-1861.807289

II.12d	DFT2	Not found	-1861.700549 -1861.814683	Not found	Not found	Not found
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Table S4. Normalization constants (α) and optimum bond lengths (R_o in Å) for CC and CN bonds applied in the HOMED procedure.^a

Bond	R_o	α_{2i}	α_{1d+2s}	α_{2d+1s}	α_{2d+3s}	α_{3d+4s}	α_{5d+6s}
CC	1.3943	88.09	72.96	111.13	78.34	80.90	83.37
CN	1.3342	91.60	76.62	113.85	81.98	84.52	86.96

^a Taken from refs. S5 and S6.

Table S5. PAs and GBs estimated for cyano and imino N atoms in isomers of investigated nitriles:.

(a) simple derivatives without big substituents

Series I Structure	N _{cyano}		Series II Structure	N _{cyano}		N(Z) _{imino}	
	PA	GB		PA	GB	PA	GB
I.1	793.3 ^a	762.7 ^a	II.1	797.4 ^a	768.0 ^a	738.3 ^a	707.1 ^a
	793.4 ^b	762.8 ^b		797.5 ^b	768.0 ^b	738.3 ^b	707.1 ^b
I.2a	834.0 ^a	805.6 ^a	II.2a	854.7 ^a	826.7 ^a	807.6 ^a	776.2 ^a
	834.1	805.6 ^b		854.7 ^b	826.7 ^b	807.6 ^b	776.3 ^b
I.2b	828.3 ^a	799.4 ^a	II.2b	851.7 ^a	824.3 ^a	815.1 ^a	783.5 ^a
	828.4 ^b	799.5 ^b		851.8 ^b	824.4 ^b	815.1 ^b	783.5 ^b
I.2c	832.0 ^a	805.8 ^a	II.2c	855.8 ^a	827.0 ^a	796.0 ^a	770.5 ^a
I.2d	822.4 ^a	791.3 ^a	II.2d	845.1 ^a	817.0 ^a	808.4 ^a	777.1 ^a
I.3	885.4 ^a	854.5 ^a	II.3	892.1 ^a	865.0 ^a	841.6 ^a	810.5 ^a
	885.5 ^b	854.6 ^b		892.1 ^b	865.0 ^b	841.7 ^b	810.6 ^b
I.4	910.1 ^a	878.4 ^a	II.4	939.3 ^a	910.5 ^a	909.3 ^a	877.7 ^a
	910.0 ^b	878.4 ^b		939.3 ^b	910.5 ^b	909.0 ^{b*}	877.5 ^{b*}
I.5	884.1 ^a	853.4 ^a	II.5	918.4 ^a	892.0 ^a	892.7 ^a	861.5 ^a
	884.1 ^b	853.4 ^a		918.5 ^b	892.0 ^b	892.6 ^b	861.4 ^b
I.6	972.9 ^a	941.6 ^a	II.6	1004.3 ^a	975.9 ^a	987.0 ^a	956.2 ^a
	972.9 ^b	941.7 ^b		1004.4 ^{b*}	975.9 ^{b*}	987.1 ^b	956.3 ^b
I.7	924.6 ^a	895.9 ^a	II.7	933.1 ^a	909.0 ^a	897.3 ^a	869.5 ^a
	924.7 ^b	895.8 ^b		933.2 ^b	908.8 ^b	897.4 ^b	869.3 ^b
I.8	971.5 ^a	939.2 ^a	II.8	975.6 ^a	943.1 ^a	935.3 ^a	901.9 ^a
	971.6 ^b	939.3 ^b		975.6 ^b	943.1 ^b	935.3 ^{b*}	902.0 ^b
I.9	998.5 ^a	972.9 ^a	II.9	1004.5 ^a	978.0 ^a	967.4 ^a	940.7 ^a
	991.1 ^b	972.7 ^b		1004.6 ^b	978.6 ^b	967.6 ^{b*}	941.8 ^b

(b) cycloprop-2-en-1-ylidene derivatives with two large substituents

Isomer	N _{cyano}		N(Z) _{imino}		N(X _{syn}) _{imin}		N(X _{anti}) _{imin}	
	PA	GB	PA	GB	PA	GB	PA	GB
I.10a	985.3 ^a	959.8 ^a	-	-	981.5 ^a	953.6 ^a	966.1 ^a	938.2 ^a
I.10b	1019.4 ^a	992.7 ^a	-	-	978.9 ^a	954.4 ^a	931.2 ^a	903.3 ^a
I.10c	993.1 ^a	968.3 ^a	-	-	947.2 ^a	920.0 ^a	970.3 ^a	944.6 ^a
II.10a	986.4 ^a	963.4 ^a	958.6 ^a	933.8 ^a	963.9 ^a	936.2 ^a	960.0 ^a	931.3 ^a
II.10b	1023.7 ^a	998.2 ^a	978.5 ^a	952.0 ^a	956.6 ^a	929.9 ^a	929.3 ^a	901.0 ^a
II.10c	999.2 ^a	978.4 ^a	992.8 ^a	967.2 ^a	928.9 ^a	901.8 ^a	957.4 ^a	929.1 ^a
I.11a	1023.2 ^b	994.3 ^b	-	-	1034.4 ^b	1001.2 ^b	1021.1 ^b	987.4 ^b
I.11b	1050.2 ^b	1016.5 ^b	-	-	1036.2 ^b	1002.0 ^b	1000.1 ^b	968.5 ^b
I.11c	1035.6 ^b	1003.7 ^b	-	-	1014.4 ^b	983.1 ^b	1021.1 ^b	987.3 ^b
II.11a	1033.5 ^b	1007.8 ^b	1017.2 ^b	988.7 ^b	1021.6 ^b	986.4 ^b	1016.2 ^b	982.0 ^b
II.11b	1061.3 ^b	1029.7 ^b	1031.8 ^b	1000.2 ^b	1019.6 ^b	984.6 ^b	993.3 ^b	961.4 ^b
II.11c	1046.8 ^b	1018.7 ^b	1041.1 ^b	1011.2 ^b	1000.6 ^b	969.0 ^b	1015.3 ^b	981.2 ^b
I.12a	1066.2 ^b	1037.8 ^b	-	-	1060.4 ^b	1026.0 ^b	1056.4 ^b	1018.4 ^b
I.12b	1088.1 ^b	1056.6 ^b	-	-	1065.0 ^b	1037.9 ^b	1029.7 ^b	998.2 ^b
I.12c	1070.5 ^b	1040.1 ^b	-	-	1042.8 ^b	1009.6 ^b	1056.4 ^b	1024.5 ^b
II.12a	1069.9 ^b	1043.1 ^b	1052.0 ^b	1020.9 ^b	1040.6 ^b	1005.6 ^b	1037.0 ^b	1002.4 ^b

II.12b	1091.5 ^b	1064.1 ^b	1066.9 ^b	1038.1 ^b	1041.4 ^b	1012.4 ^b	1020.1 ^b	992.4 ^b
II.12c	-	-	1072.6 ^b	1041.7 ^b	1024.0 ^b	991.5 ^b	10.42.8 ^b	1012.6 ^b

^a B3LYP/6-311+G(d,p). ^b B3LYP/6-311++G(d,p).

Rotation about the single C–X bond of the two large substituents in disubstituted neutral derivatives affects intramolecular interactions in the possible four isomers, and consequently, changes their stabilities and relative Gibbs energies (Chart S2). These interactions are not of the same type, and isomeric preferences change when proceeding from one large substituent to the other ones. Exceptionally, the isomer **c**, stabilized by two favorable intramolecular interactions between acid and base groups ($\text{NH}\cdots\text{N}\equiv\text{C}$ and $\text{NH}\cdots\text{N}=\text{C}$), is favored at the DFT1 level for the CH derivative **I.10** with two $\text{N}=\text{C}(\text{NH}_2)_2$ (Fig. S1), whereas two isomers **a** and **c**, each stabilized by interacting CH_3 and $\text{C}\equiv\text{N}$ groups, predominate for isomers of the CH derivative **I.11** with two $\text{N}=\text{C}(\text{NMe}_2)_2$ at the DFT2 level (Fig. S2). For the CH derivative **I.12** with two $\text{N}=\text{P}(\text{NMe}_2)_3$, two isomers **a** and **c**, exhibiting analogous $\text{H}_2\text{C}-\text{H}\cdots\text{N}\equiv\text{C}$ interactions (Fig. S2), are also favored, but their relative Gibbs energies are reverse to those for **I.11** with two $\text{N}=\text{C}(\text{NMe}_2)_2$ (Chart S2). Introduction of the imino N atom (Z) in the diguanidino derivatives **II.10** and **II.11**, and in the diphosphazeno **II.12** derivatives favors only one isomer **a**. Note that the isomer **d** is not found for diguanidino and diphosphazeno derivatives. It is unstable, and during optimization a substituent conformation changes, and the isomer **d** transforms into one of the other stable isomers. Analogous type of C–H \cdots N interactions has been discussed in the literature for 1-(2-hydroxyiminopyranosyl)-pyrazoles⁵⁷ and 2,3-dithiazolylindole.⁵⁸

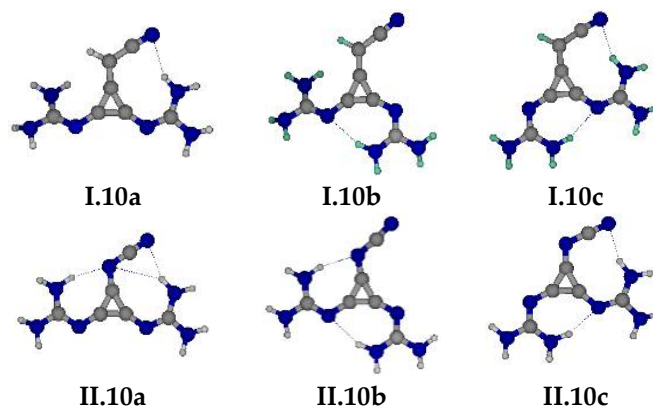


Figure S1. Possible intramolecular interactions in neutral isomers **I.10a-c** and **II.10a-c** containing two unsubstituted guanidine groups.

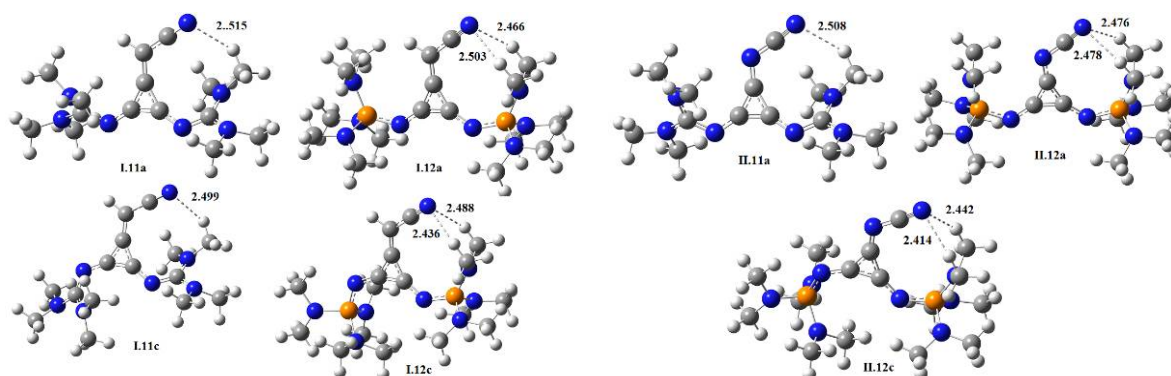


Figure S2. Possible intramolecular $\text{H}_2\text{C}-\text{H}\cdots\text{N}$ interactions in the DFT2-optimized structures of neutral isomers **I.11a**, **I.11c**, and **II.11a** containing two tetramethylguanidine groups, and **I.12a**, **I.12c**, **II.12a**, and **II.12c** with two hexamethylphosphazene groups. The hydrogen bond distances are in (Å).

For the cyano N-protonated diguanidino derivative **I.10**, the isomer **b** has the lowest Gibbs energy, while the isomer **c** is less stable by 3 kJ mol⁻¹ at the DFT1 level (Chart S3). Both isomers can be stabilized by possible intramolecular interaction between the amino NH of one X and the imino N of the other X, but some repulsion possible in **c** between C≡NH⁺ and NH₂ (amino group partially and positively charged due to stronger pushing effect in the H-bonded guanidine group) can explain its lower stability (Fig. S3). Similar trend takes place for **II.10**, however, the relative Gibbs energy between **c** and **b** is higher (15 kJ mol⁻¹), because more favorable intramolecular interactions NH...N=C are possible for **b** than **c**. The distance between NH and N(Z)=C in **c** is considerably longer (2.979 Å) than that in **b** (2.439 Å). Moreover, the geometry-contact of NH and N(Z)=C in **c** does not seem to be typical for the intramolecular H-bond.

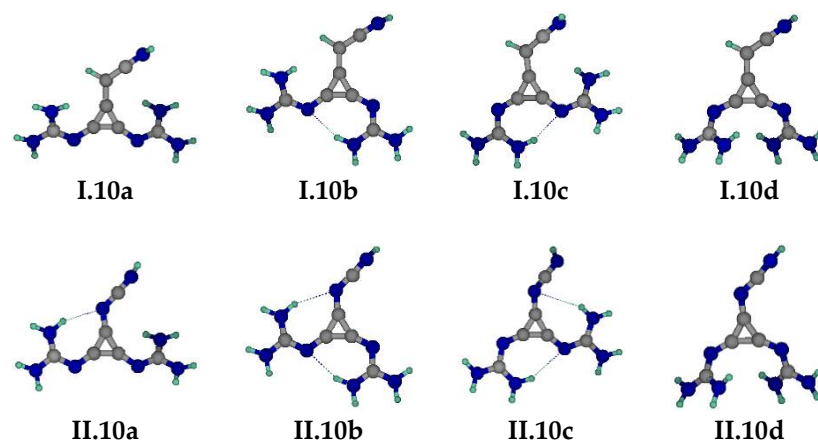


Figure S3. Intramolecular interactions possible in cyano N protonated isomers **I.10a-d** and **II.10a-d** possessing two unsubstituted guanidine groups.

Protonation of the cyano N atom strongly affects the Z=C and Z-CN bond lengths (Table T6). The Z=C bond lengthens and the ZCN bond shortens owing to resonance effects.

Table S6. Variations of Z=C and Z-CN bonds lengths (in Å) for simple conjugated nitriles when going from the neutral to cyano N protonated forms calculated at the DFT1 level.

Compound	Neutral		Protonated		Compound	Neutral		Protonated	
	Z=C	Z-CN	Z=C	Z-CN		Z=C	Z-CN	Z=C	Z-CN
I.1	1.335	1.428	1.344	1.405	II.1	1.276	1.339	1.283	1.287
I.2a	1.348	1.421	1.369	1.384	II.2a	1.289	1.332	1.312	1.269
I.2b	1.349	1.423	1.370	1.385	II.2b	1.290	1.333	1.308	1.265
I.3	1.342	1.418	1.379	1.361	II.3	1.279	1.335	1.304	1.265
I.4	1.375	1.412	1.431	1.343	II.4	1.319	1.321	1.364	1.240
I.5	1.368	1.414	1.411	1.353	II.5	1.310	1.324	1.343	1.244
I.6	1.375	1.411	1.434	1.336	II.6	1.319	1.320	1.371	1.234
I.7	1.349	1.416	1.395	1.350	II.7	1.289	1.333	1.321	1.255
I.8	1.362	1.410	1.415	1.337	II.8	1.301	1.328	1.338	1.243
I.9	1.367	1.408	1.423	1.331	II.9	1.308	1.324	1.349	1.237
I.10a	1.372	1.405	1.426	1.332	II.10a	1.322	1.319	1.361	1.237
I.10b	1.361	1.412	1.419	1.336	II.10b	1.307	1.328	1.356	1.242
I.10c	1.367	1.404	1.423	1.330	II.10c	1.312	1.316	1.350	1.229

When we plot the PAs calculated for various simple Z (CH and N) series of nitriles: $XCH=Z-C\equiv N$ and $X_2C=Z-C\equiv N$ (X: H, NH_2 , and NMe_2) studied previously,⁵⁹ and $X_2C_2C=Z-C\equiv N$ {X: H (3), Me (7), NH_2 (8), and NMe_2 (9)} and cyclo- $C_xH_yC=Z-C\equiv N$ (with group 4-6 given in Fig. 1) examined in this work, we can distinguish two subfamilies (Fig. S4). One subfamily contains series of simple mono- $XCH=Z-C\equiv N$ and disubstituted nitriles $X_2C=Z-C\equiv N$, as well as derivatives with cyclopropene-transmitter $X_2C_2C=Z-C\equiv N$ (3, 7-9 in Fig. 1) The other one refers to series cyclo- $C_xH_yC=Z-C\equiv N$ containing larger π -electron cyclic groups (4, 5, and 6 in Fig. 1). Nevertheless, the slopes of regression lines and correlation coefficients (*R*) are close to unity for both subfamilies.

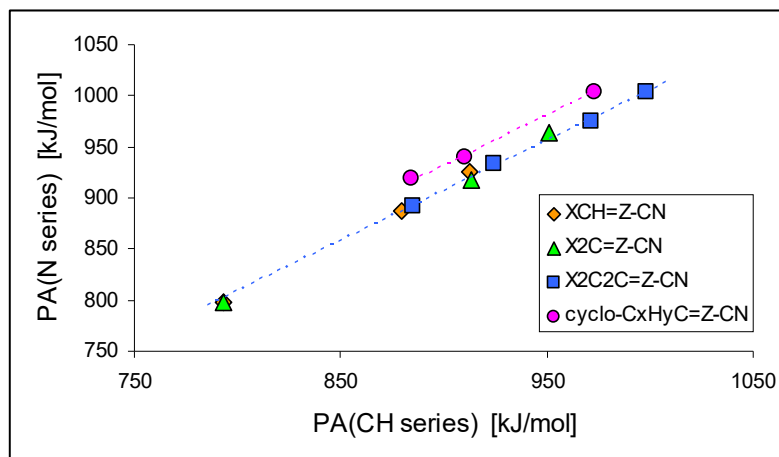


Figure S4. Linear relations between PAs for various simple Z (CH and N) series of nitriles: $XCH=Z-C\equiv N$ and $X_2C=Z-C\equiv N$ (X: H, NH_2 , and NMe_2) studied previously,⁵⁹ and $X_2C_2C=Z-C\equiv N$ {X: H (3), Me (7), NH_2 (8), and NMe_2 (9)} and cyclo- $C_xH_yC=Z-C\equiv N$ (with group 4-6 given in Fig. 1) examined in this work.

On the other hand, when we plot (Fig. S5) the calculated PAs of series $X_2C_2C=Z-C\equiv N$ investigated here against those of $X_2C=Z-C\equiv N$ studied previously⁵⁹ (X: H, NH_2 , and NMe_2), both containing two substituents X, the slope of the linear relationship ($R = 0.9995$) is smaller than unity (0.698). The cyclopropene group attenuates the substituent X effects by ca. 70 %.

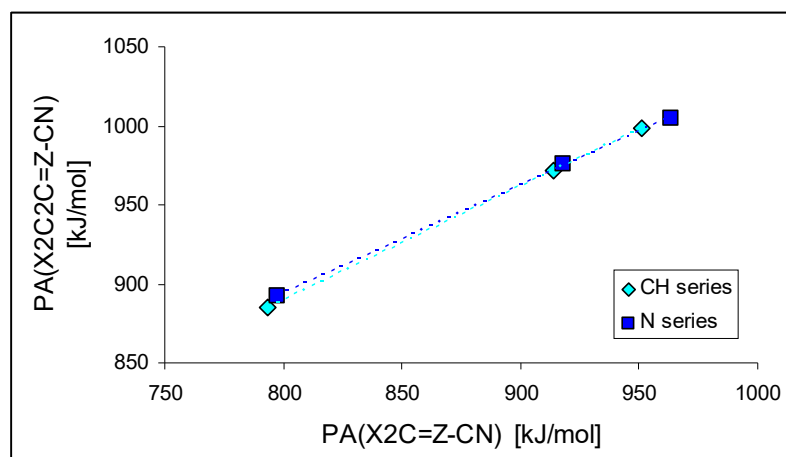
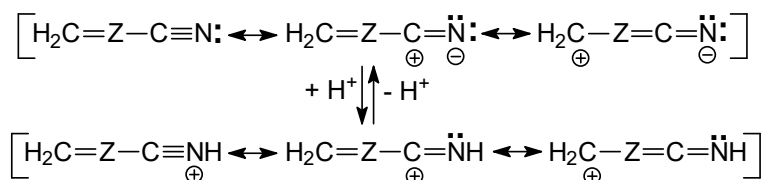


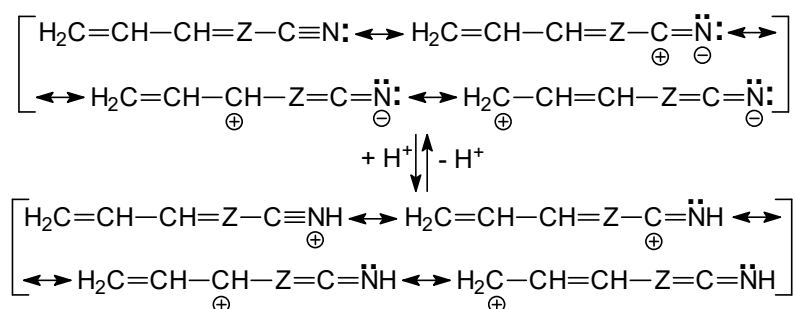
Figure S5. Linear relations between PAs of series $X_2C_2C=Z-C\equiv N$ investigated here and $X_2C=Z-C\equiv N$ studied previously⁵⁹ (X: H, NH_2 , and NMe_2).

The changes in bonds lengths when going from the neutral to cyano N protonated compounds may be explained by differences in resonance hybrids for both species (Scheme S1 in SM). For neutral molecules, we can write only one resonance structure without charge separation and numerous resonance structures with separation of positive and negative charge. In the case of monocations, potential resonance structures contain the positive charge. The resonance structures differ by positions of delocalized electrons (σ and/or π), and consequently, by position of the positive charge. Delocalization of electrons and charge affect the dihedral angle ZCNH that it is lower than 180° for the cyano N protonated forms. According to the well-recognized theory of resonance, participation of resonance structures with separation of charge (positive and negative) in the resonance hybrid is lower than those without this separation. Hence, for the neutral form only one resonance structure (without charge separation) can significantly participate in the resonance hybrid, whereas for the protonated form all resonance structures can take part in the resonance hybrid with higher contribution of those containing positive charge outside of the cyano group. The same is true for other conjugated N bases such as amidines, guanidines, biguanides, phosphazenes, etc., for which analogous differences occur between resonance hybrids of neutral and protonated compounds.^{S10}

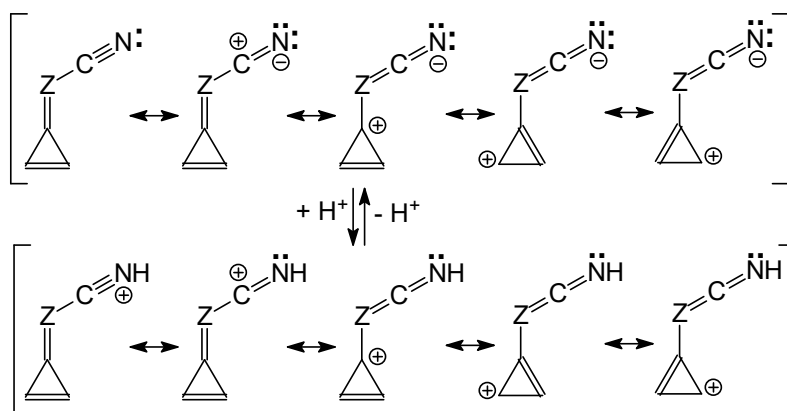
a) I.1 (Z: CH) and II.1 (Z: N)



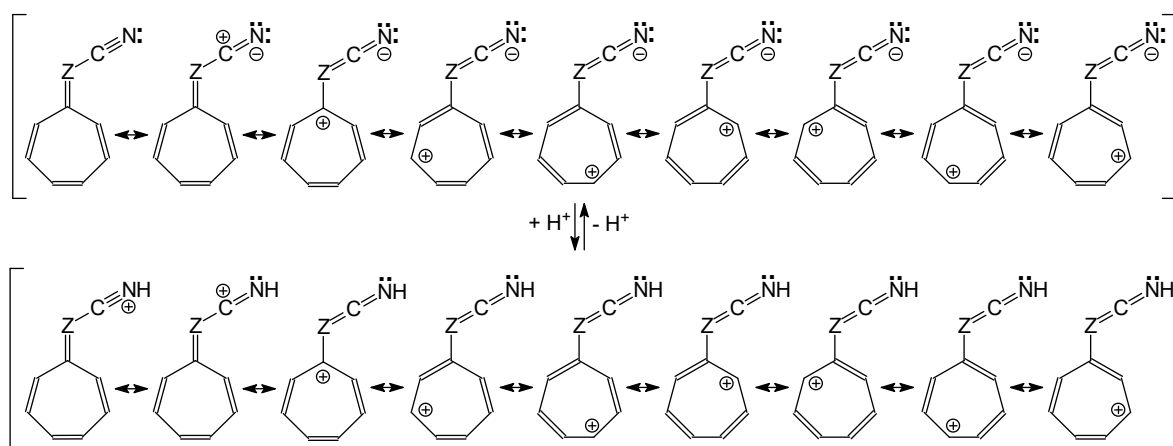
b) I.2 (Z: CH) and II.2 (Z: N)



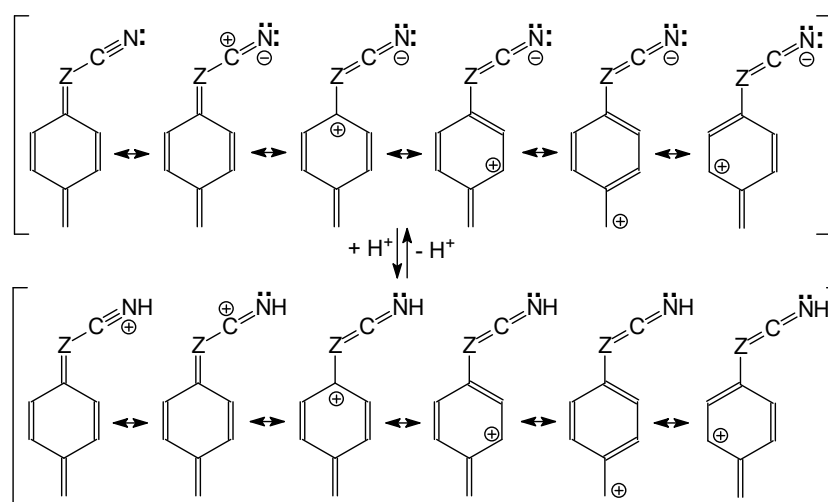
c) I.3 (Z: CH) and II.3 (Z: N)



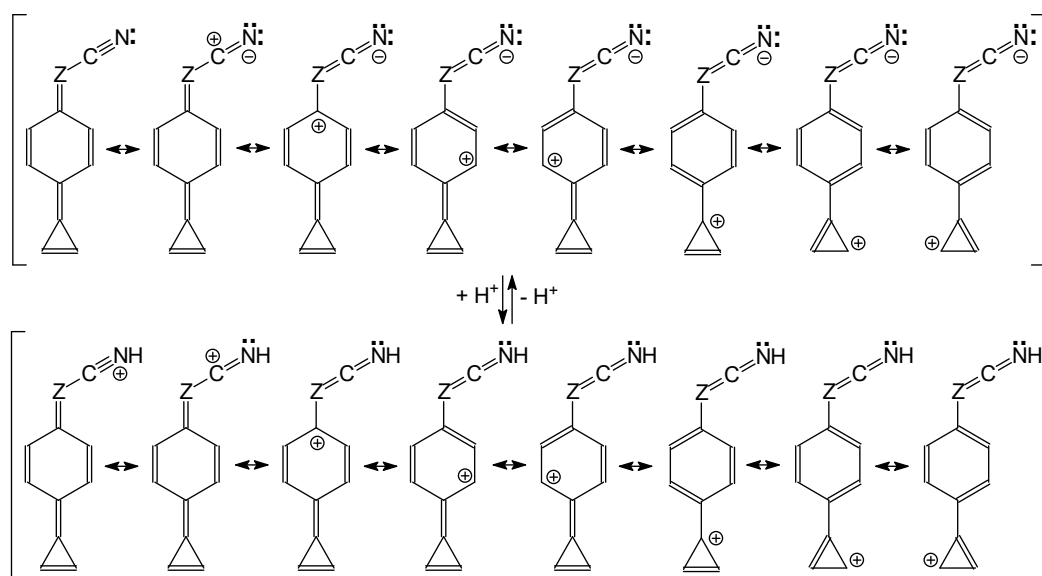
d) I.4 (Z: CH) and II.4 (Z: N)



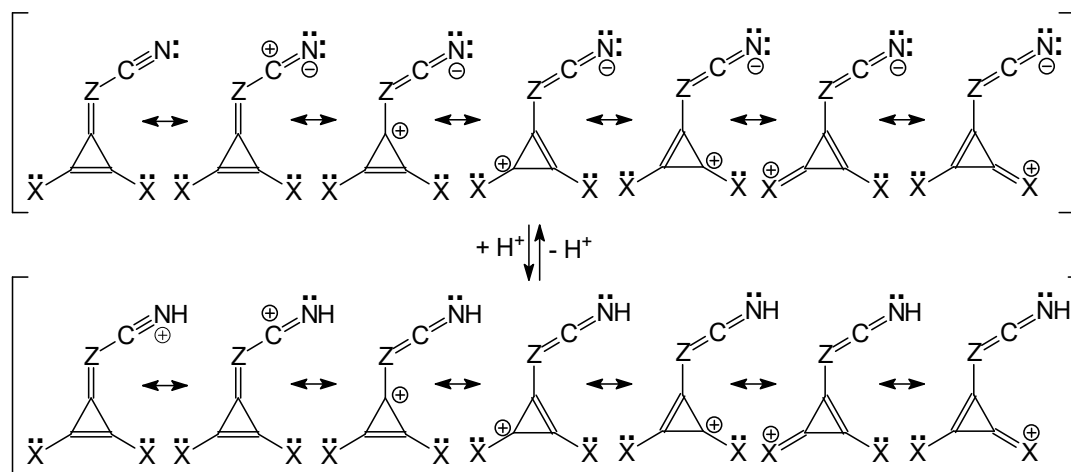
e) I.5 (Z: CH) and II.5 (Z: N)



f) I.6 (Z: CH) and II.6 (Z: N)

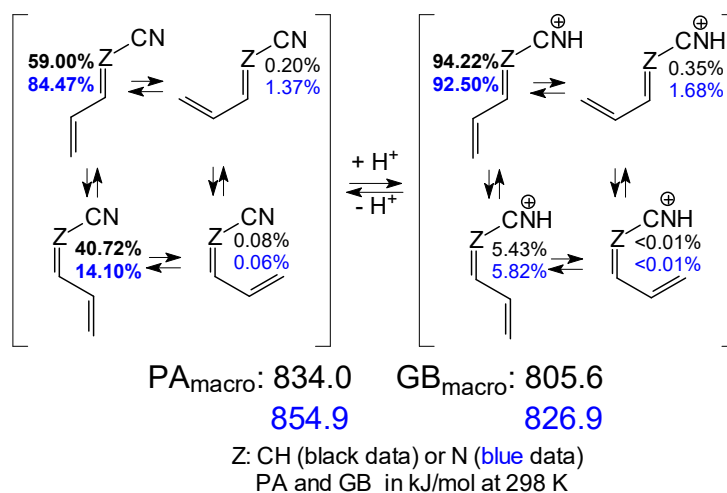
**Scheme S1.** Potential resonance structures for neutral and cyano N protonated simple nitriles.

For CPC and CPN derivatives (**I.7-I.12** and **II.7-II.12**), substituents X also take part in electron and charge delocalization (Scheme S2).

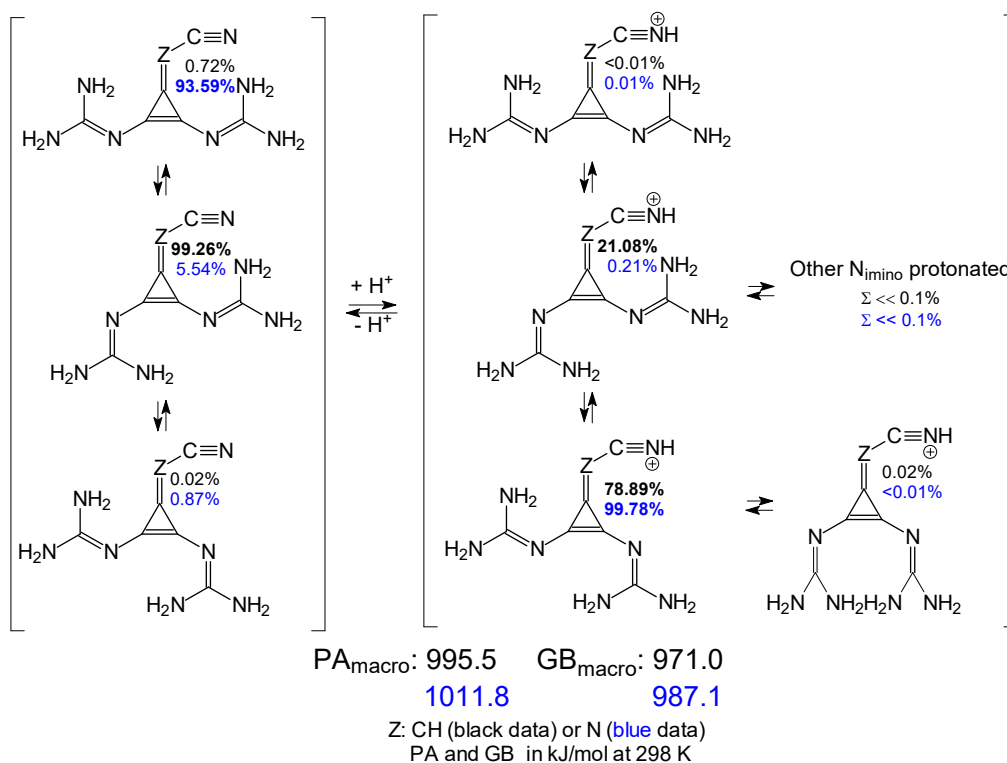


Scheme S2. Selected resonance structures for neutral and cyano N protonated methylenecyclopropene and cyclopropenimine derivatives.

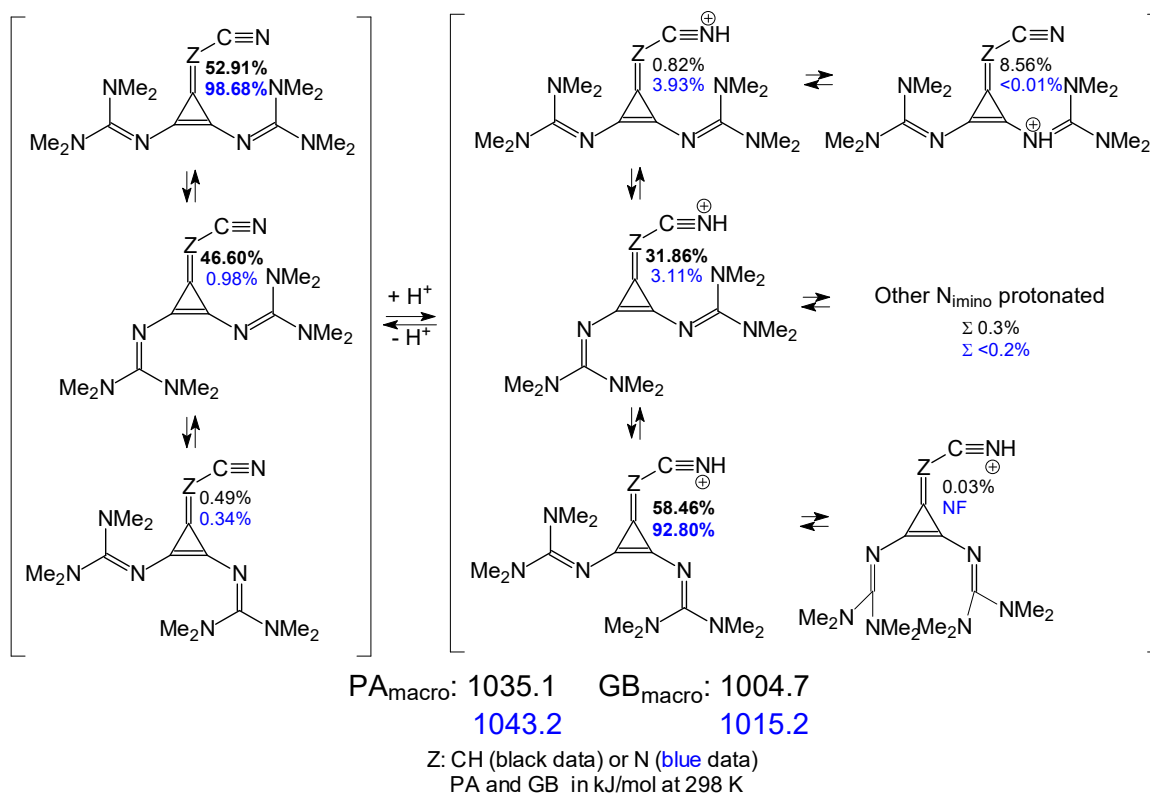
The macroscopic PAs and GBs were estimated for nitriles displaying isomerism (**I.2**, **II.2**, **I.10-I.12**, and **II.10-II.12**). For estimations, the percentage contents of potential isomers present in the isomeric mixtures were taken into account for the neutral and monoprotinated forms as given in Schemes S3-S6.



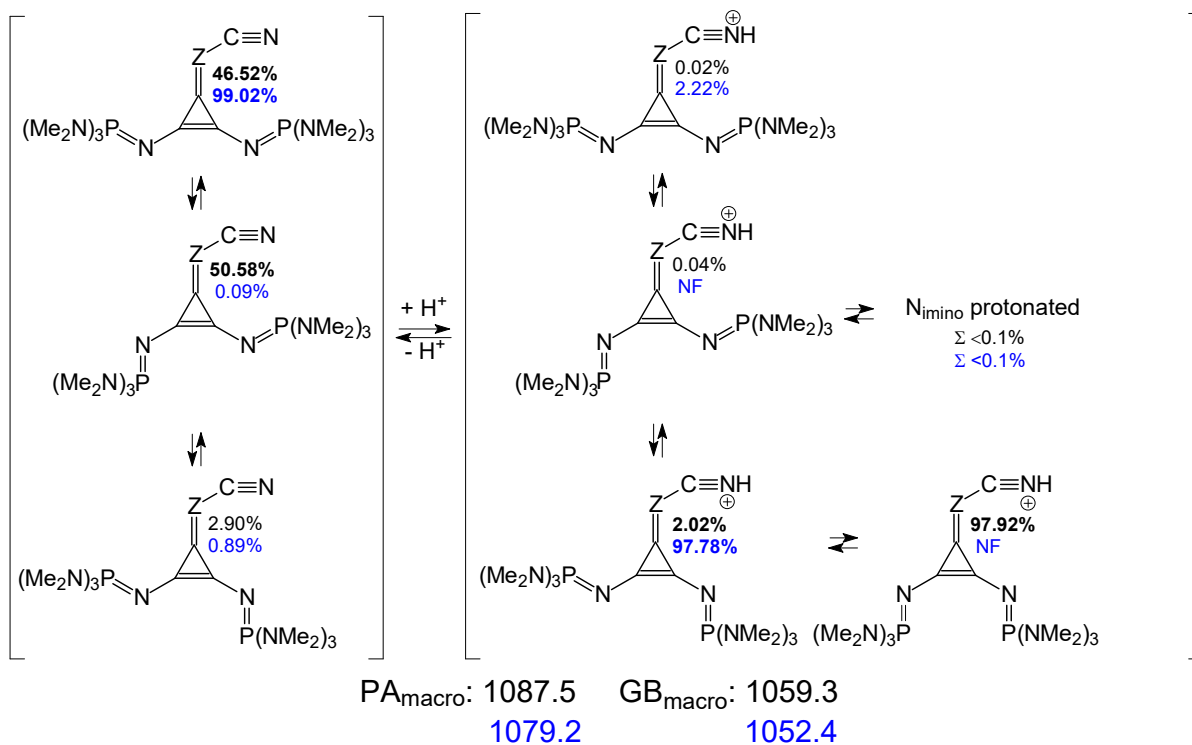
Scheme S3. Monoprotonation reaction for isomeric mixture of **I.2** (Z: CH) and **II.2** (Z: N), percentage contents of individual isomers, and DFT1-estimated macroscopic PAs and GBs (in kJ mol⁻¹ at 298 K).



Scheme S4. Monoprotonation reaction for isomeric mixture of **I.10** (Z: CH) and **II.10** (Z: N), percentage contents of individual isomers, and DFT1-estimated macroscopic PAs and GBs (in kJ mol⁻¹ at 298 K).



Scheme S5. Monoprotonation reaction for isomeric mixture of **I.11** (Z: CH) and **II.11** (Z: N), percentage contents of individual isomers, and DFT2-estimated macroscopic PAs and GBs (in kJ mol⁻¹ at 298 K).



Z: CH (black data) or N (blue data)
 PA and GB in kJ/mol at 298 K

Scheme S6. Monoprotonation reaction for isomeric mixture of **I.12** (Z: CH) and **II.12** (Z: N), percentage contents of individual isomers, and DFT2-estimated macroscopic PAs and GBs (in kJ mol⁻¹ at 298 K).

References

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