Supplementary Material (ESI) for New Journal of Chemistry

SUPPORTING INFORMATION

Rees polycyanated hydrocarbons and related compounds are extremely powerful Brønsted superacids in the gas-phase and DMSO – a density functional B3LYP study

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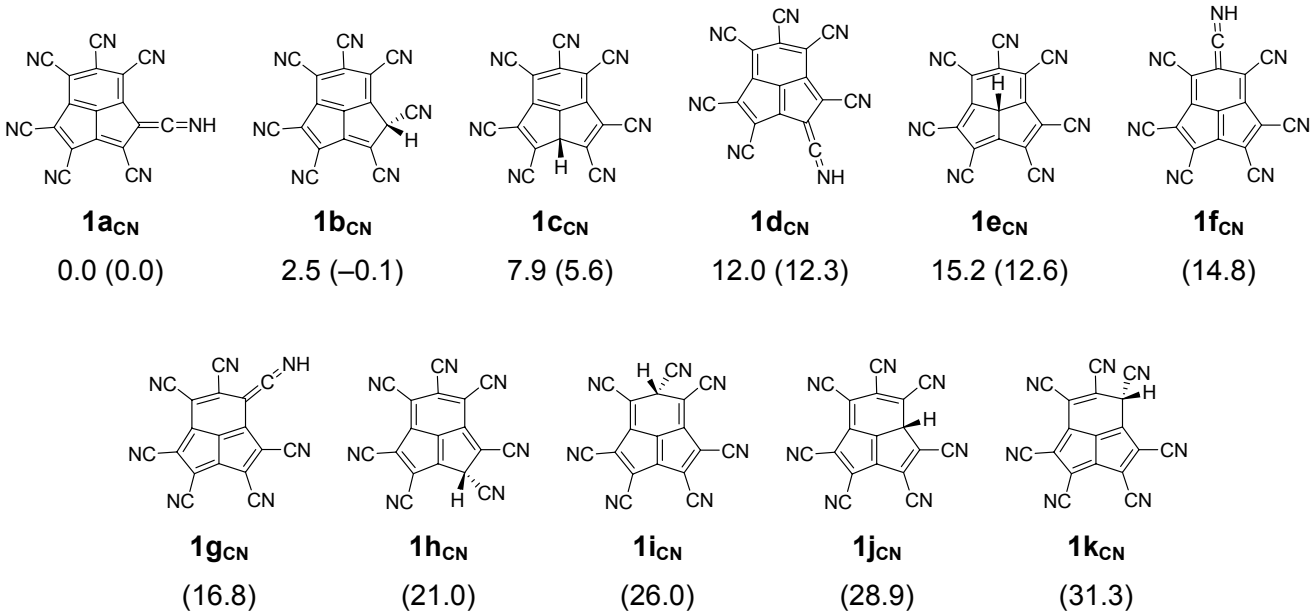


Figure S1. Schematic representation of heptacyano-7b*H*-cyclopenta[*cd*]indene tautomers and their relative energies obtained by the B3LYP/6–311+G(2d,p)//B3LYP/6–31G(d) and B3LYP/6–31G(d) models. The latter are given within parentheses (in kcal mol^{-1}).

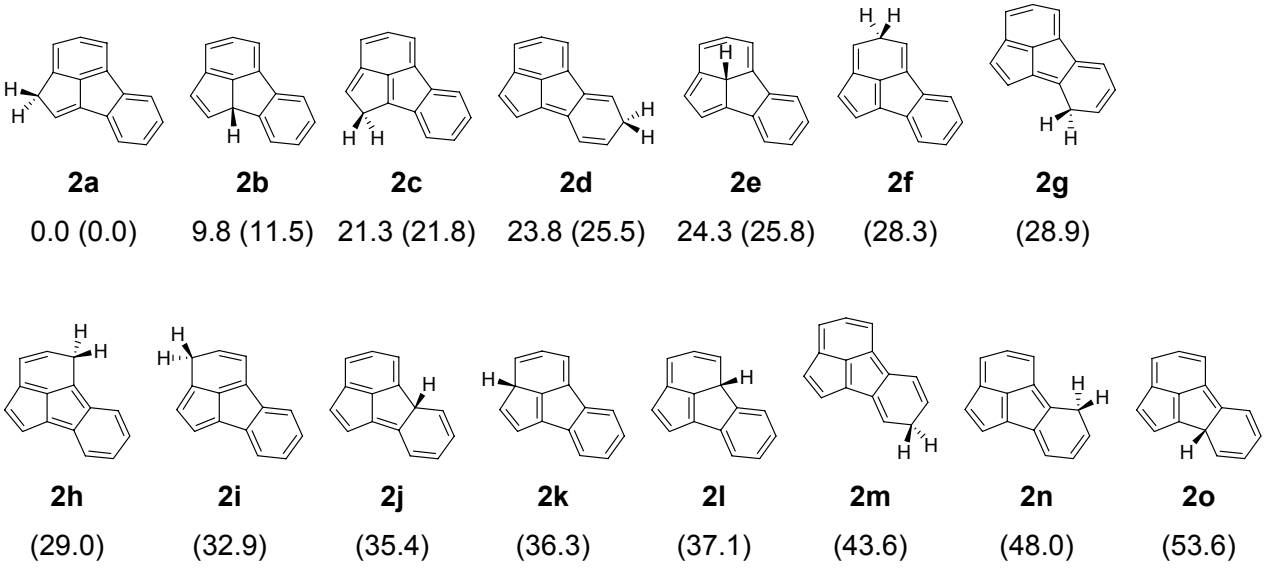
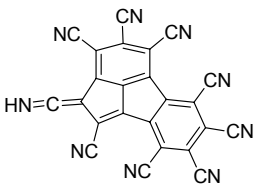
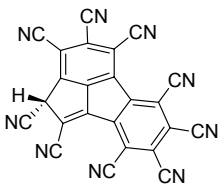


Figure S2. Schematic representation of 9c*H*-cyclopenta[*jk*]fluorene tautomers and their relative energies obtained by the B3LYP/6–311+G(2d,p)//B3LYP/6–31G(d) and B3LYP/6–31G(d) models. The latter are given within parentheses (in kcal mol^{-1}).



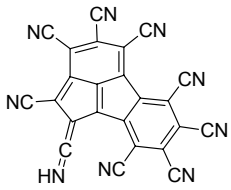
2a$_{CN}$

0.0 (0.0)



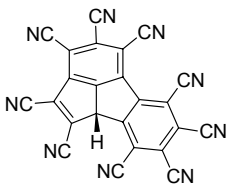
2b$_{CN}$

3.4 (0.9)



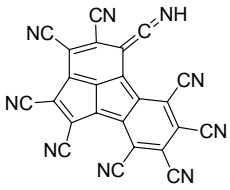
2c$_{CN}$

7.8 (8.0)



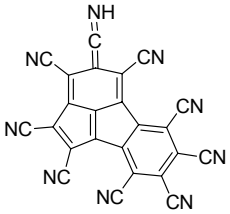
2d$_{CN}$

8.8 (6.7)



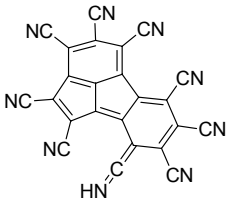
2e$_{CN}$

11.3 (11.9)



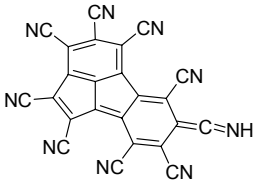
2f$_{CN}$

12.8 (13.6)



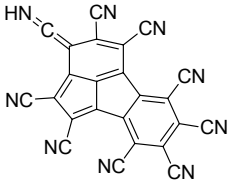
2g$_{CN}$

13.2 (13.5)



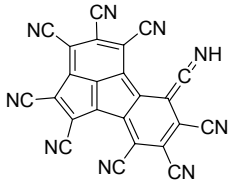
2h$_{CN}$

13.8 (14.5)



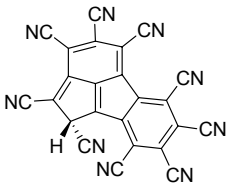
2i$_{CN}$

16.0 (16.8)



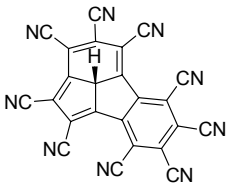
2j$_{CN}$

17.6 (18.5)



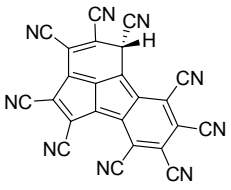
2k$_{CN}$

20.7 (18.5)



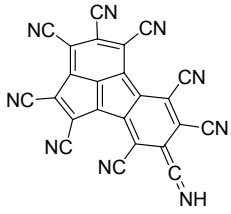
2l$_{CN}$

22.4 (20.3)



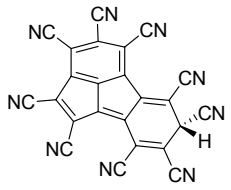
2m$_{CN}$

(22.9)



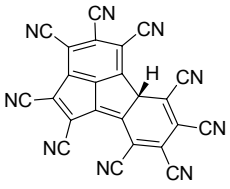
2n$_{CN}$

(23.1)



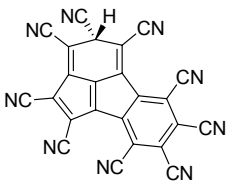
2o$_{CN}$

(23.2)



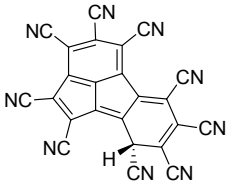
2p$_{CN}$

(24.0)



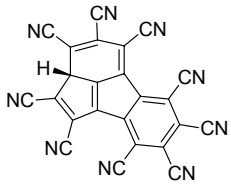
2q$_{CN}$

(24.2)



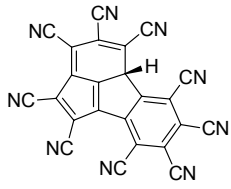
2r$_{CN}$

(26.2)



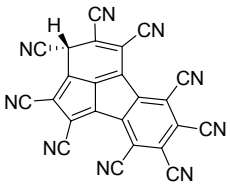
2s$_{CN}$

(27.2)

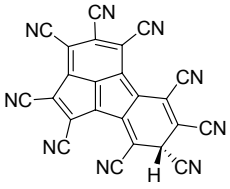


2t$_{CN}$

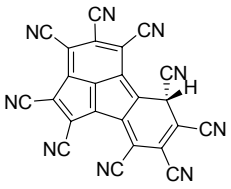
(28.3)



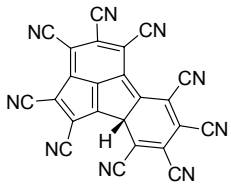
2u$_{CN}$



2w$_{CN}$



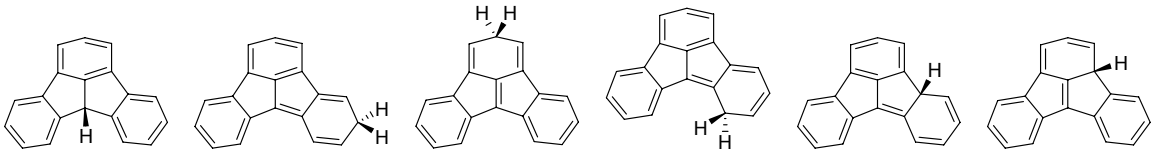
2y$_{CN}$



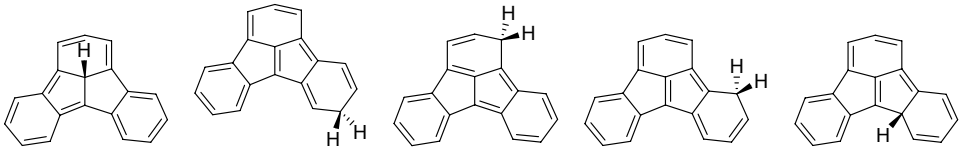
2x$_{CN}$

(31.0) (40.8) (41.5) (43.0)

Figure S3. Prototropic tautomerism in nonacyano-9c*H*-cyclopenta[*jk*]fluorene. The relative stabilities (in kcal mol^{-1}) are calculated by the B3LYP/6–311+G(2d,p)//B3LYP/6–31G(d) (B3LYP/6–31G(d)) methods.

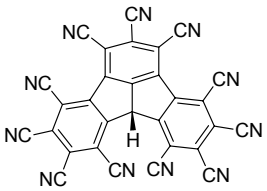


3a	**3b**	**3c**	**3d**	**3e**	**3f**
0.0 (0.0)	15.3 (14.4)	16.6 (15.8)	18.6 (17.5)	24.2 (24.3)	24.2 (24.8)



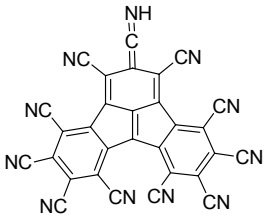
3g	**3h**	**3i**	**3j**	**3k**
27.8 (28.0)	(31.9)	(32.8)	(36.3)	(41.6)

Figure S4. Schematic representation of fluoradene tautomers and their relative energies obtained by the B3LYP/6–311+G(2d,p)//B3LYP/6–31G(d) and B3LYP/6–31G(d) models. The latter are given within parentheses (in kcal mol^{-1}).



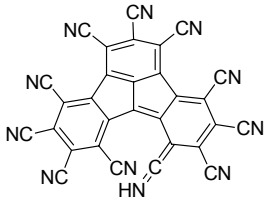
$3a_{CN}$

0.0 (0.0)



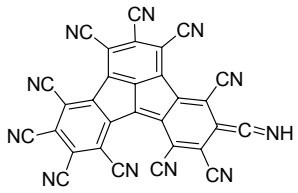
$3b_{CN}$

2.7 (7.1)



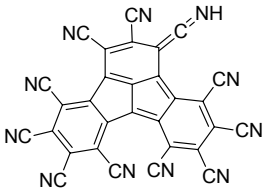
$3c_{CN}$

3.1 (6.7)



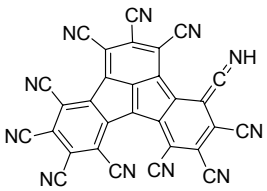
$3d_{CN}$

3.5 (7.8)



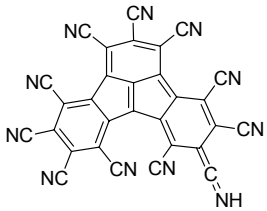
$3e_{CN}$

6.4 (10.9)



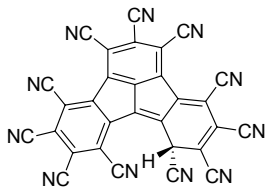
$3f_{CN}$

8.7 (12.7)



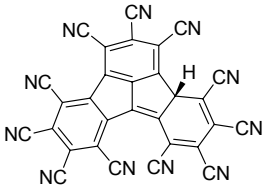
$3g_{CN}$

10.8 (15.3)



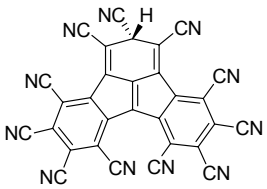
$3h_{CN}$

12.1 (12.9)



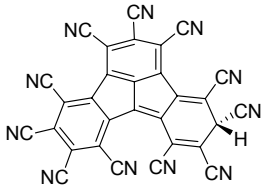
$3i_{CN}$

14.3 (15.6)



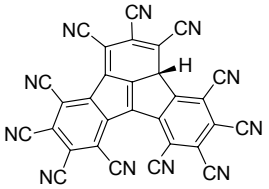
$3j_{CN}$

14.3 (16.1)



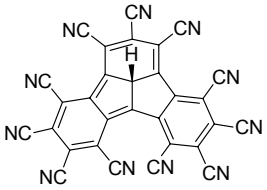
$3k_{CN}$

14.9 (16.2)



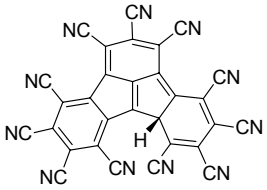
$3l_{CN}$

18.0 (19.8)



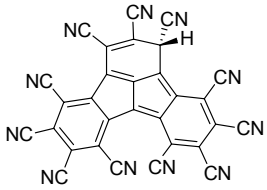
$3m_{CN}$

25.4 (26.0)



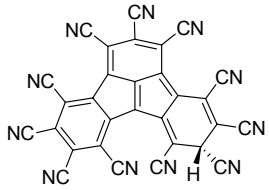
$3n_{CN}$

(30.0)



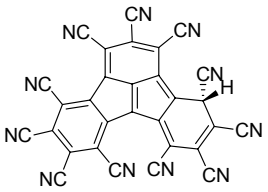
$3o_{CN}$

(30.6)



$3p_{CN}$

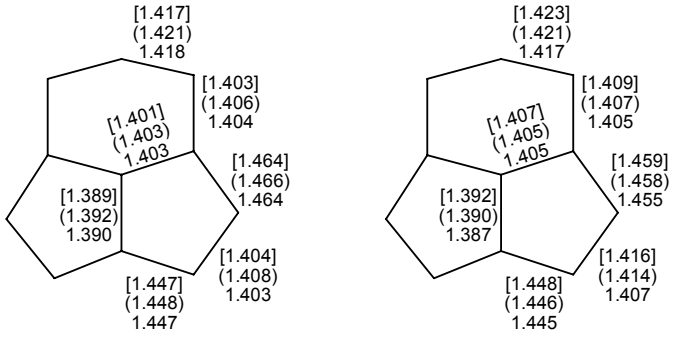
(31.5)



$3q_{CN}$

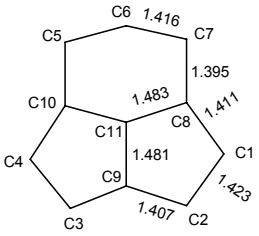
(33.1)

Figure S5. Prototropic tautomerism in undecacyano-fluoradene. The relative stabilities (in kcal mol^{-1}) are calculated by the B3LYP/6–311+G(2d,p)//B3LYP/6–31G(d) and (B3LYP/6–31G(d)) methods.

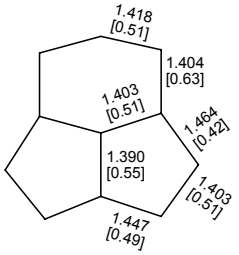


B3LYP data MP2 data

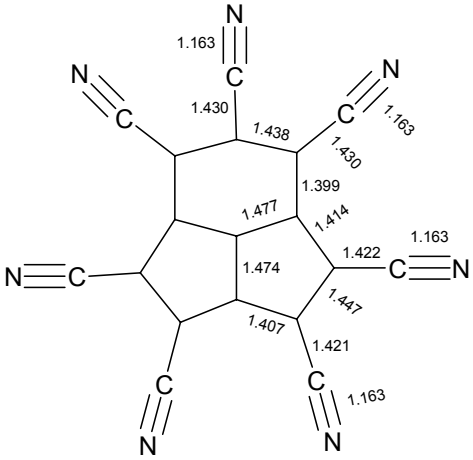
Figure S6. Relevant geometrical parameters of **1**$^{-}$ obtained with B3LYP and MP2 methodologies employing 6–31G(d), (6–31+G(d)) and [6–311+G(d,p)] basis sets.



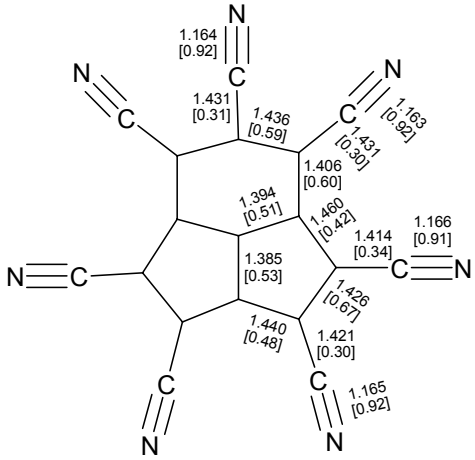
1c



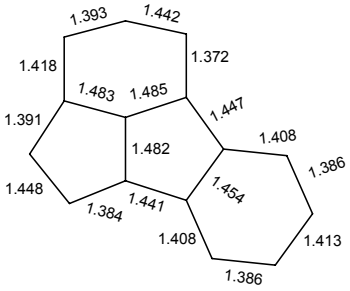
1⁻



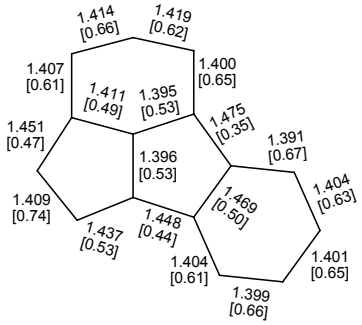
1e$_{CN}$



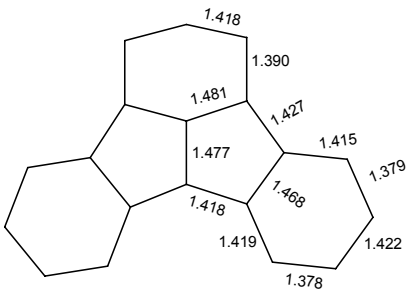
1$_{CN}$⁻

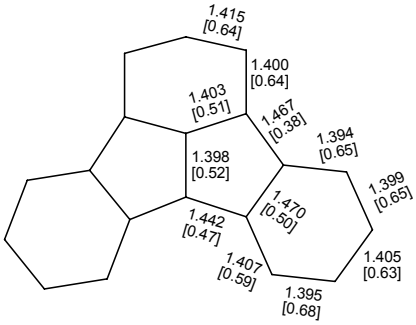


2e



2⁻





3g **3^-**

Figure S7. Schematic representation and numbering of atoms in **1c**, its heptacyano derivative **$1e_{CN}$** and systems **2e** and **3g** as well as their anions **1^-**, **1_{CN}^-**, **2^-** and **3^-**. Characteristic bond lengths (in Å) are computed by the B3LYP/6–31G(d) model. Löwdin π–bond orders in the planar anions are given within the squared parentheses and are obtained by the HF/6–31G(d)//B3LYP/6–31G(d) approach.

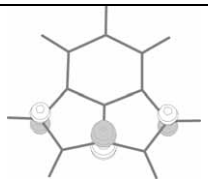
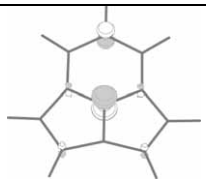
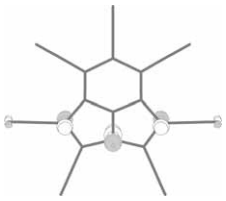
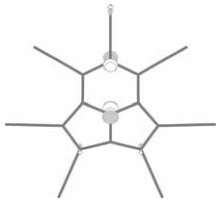
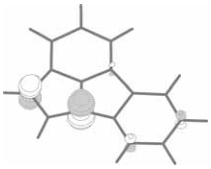
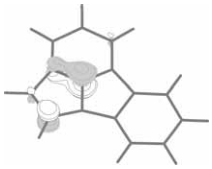
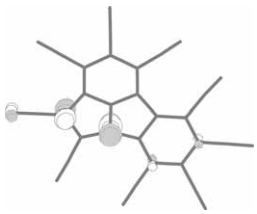
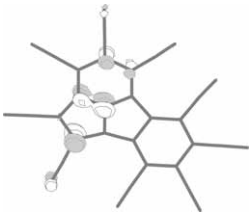
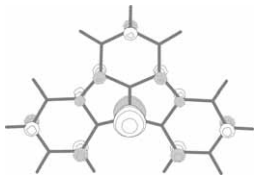
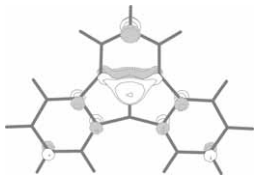
system	HOMO	HOMO–1
$\mathbf{1}^-$		
	$(-0.07833)_{\mathbf{1a}}$	$(-0.11290)_{\mathbf{1c}}$
$\mathbf{1}_{CN}^-$		
	$(-0.22620)_{\mathbf{1aCN}}$	$(-0.25832)_{\mathbf{1eCN}}$
$\mathbf{2}^-$		
	$(-0.08080)_{\mathbf{2a}}$	$(-0.12507)_{\mathbf{2e}}$
$\mathbf{2}_{CN}^-$		
	$(-0.22954)_{\mathbf{2aCN}}$	$(-0.26478)_{\mathbf{2lCN}}$
$\mathbf{3}^-$		
	$(-0.08077)_{\mathbf{3a}}$	$(-0.13916)_{\mathbf{3g}}$
$\mathbf{3}_{CN}^-$		
	$(-0.23078)_{\mathbf{3aCN}}$	$(-0.28288)_{\mathbf{3mCN}}$

Figure S8. Selected molecular orbitals together with their orbital energies [HF/6–311+G(2d,p)//B3LYP/6–31G(d) results; in a.u.] for anions discussed in the text. PRIMO orbitals are given within round brackets with subscripts denoting corresponding neutral acid.

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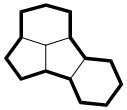
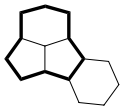
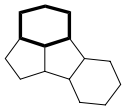
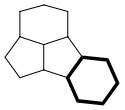
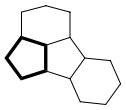
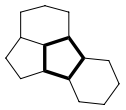
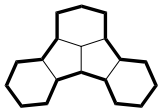
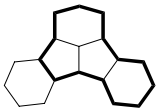
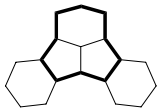
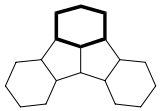
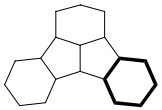
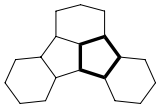
Table S1. Geometrical parameters and NICS indices for selected acids and their deprotonated forms.[a,b] Chemical bonds taken into account are given in bold, while their number is given as a subscript next to the HOMA index.

								
system	**1a**	**1$^-$**	**1a**	**1$^-$**	**1a**	**1$^-$**	**1a**	**1$^-$**
HOMA	$(0.848)_{10}$	$(0.452)_{10}$	$(0.153)_6$	$(0.881)_6$	$(-0.020)_5$	$(0.499)_5$	$(-0.020)_5$	$(0.499)_5$
$L(d)_{CC}$	0.015	0.045						
$L(d)_{CC}$/ %	10.7	32.3						
NICS(1)				-14.5		-6.7		-6.7
$NICS(1)_{zz}$				-36.0		-11.3		-11.3
system	**1a$_{CN}$**	**1$_{CN}^-$**	**1a$_{CN}$**	**1$_{CN}^-$**	**1a$_{CN}$**	**1$_{CN}^-$**	**1a$_{CN}$**	**1$_{CN}^-$**
HOMA	$(0.630)_{10}$	$(0.384)_{10}$	$(0.094)_6$	$(0.771)_6$	$(-0.024)_5$	$(0.517)_5$	$(-0.024)_5$	$(0.517)_5$
$L(d)_{CC}$	0.034	0.028						
$L(d)_{CC}$/ %	24.3	20.1						
NICS(1)				-14.3		-6.4		-6.4
$NICS(1)_{zz}$				-31.8		-6.9		-6.9

												
system	**2a**	**2$^-$**	**2a**	**2$^-$**	**2a**	**2$^-$**	**2a**	**2$^-$**	**2a**	**2$^-$**	**2a**	**2$^-$**
HOMA	$(0.716)_{14}$	$(0.615)_{14}$	$(0.527)_{10}$	$(0.312)_{10}$	$(0.032)_6$	$(0.883)_6$	$(0.751)_6$	$(0.683)_6$	$(0.077)_5$	$(0.618)_5$	$(-0.241)_5$	$(0.080)_5$
$L(d)_{CC}$	0.043	0.039										
$L(d)_{CC}$/ %	30.7	28.1										
NICS(1)						-14.3	-13.0	-11.0		-8.8		-5.9
$NICS(1)_{zz}$						-35.2	-31.4	-25.8		-17.5		-6.8
system	**2a$_{CN}$**	**2$_{CN}^-$**	**2a$_{CN}$**	**2$_{CN}^-$**	**2a$_{CN}$**	**2$_{CN}^-$**	**2a$_{CN}$**	**2$_{CN}^-$**	**2a$_{CN}$**	**2$_{CN}^-$**	**2a$_{CN}$**	**2$_{CN}^-$**
HOMA	$(0.525)_{14}$	$(0.518)_{14}$	$(0.313)_{10}$	$(0.230)_{10}$	$(-0.130)_6$	$(0.769)_6$	$(0.683)_6$	$(0.581)_6$	$(-0.237)_5$	$(0.625)_5$	$(-0.542)_5$	$(0.085)_5$
$L(d)_{CC}$	0.045	0.032										

$L(d)_{CC}$/ %	32.3	22.8										
NICS(1)						-14.0	-13.4	-11.1		-8.9		-5.5
$NICS(1)_{zz}$						-30.3	-28.1	-21.4		-14.1		-3.2
												
system	**3a**	**3^-**	**3a**	**3^-**	**3a**	**3^-**	**3a**	**3^-**	**3a**	**3^-**	**3a**	**3^-**
HOMA	$(0.818)_{18}$	$(0.688)_{18}$	$(0.704)_{14}$	$(0.491)_{14}$	$(0.499)_{10}$	$(0.136)_{10}$	$(0.179)_{6}$	$(0.906)_{6}$	$(0.595)_{6}$	$(0.674)_{6}$	$(-0.309)_{5}$	$(0.165)_{5}$
$L(d)_{CC}$	0.033	0.037										
$L(d)_{CC}$/ %	23.9	26.2										
NICS(1)								-14.4	-11.5	-11.4		-7.8
$NICS(1)_{zz}$								-35.4	-25.9	-26.9		-12.4
system	**$3a_{CN}$**	**3_{CN}^-**	**$3a_{CN}$**	**3_{CN}^-**	**$3a_{CN}$**	**3_{CN}^-**	**$3a_{CN}$**	**3_{CN}^-**	**$3a_{CN}$**	**3_{CN}^-**	**$3a_{CN}$**	**3_{CN}^-**
HOMA	$(0.688)_{18}$	$(0.598)_{18}$	$(0.575)_{14}$	$(0.428)_{14}$	$(0.399)_{10}$	$(0.121)_{10}$	$(-0.016)_{6}$	$(0.768)_{6}$	$(0.432)_{6}$	$(0.607)_{6}$	$(-0.271)_{5}$	$(0.231)_{5}$
$L(d)_{CC}$	0.030	0.030										
$L(d)_{CC}$/ %	21.3	21.5										
NICS(1)												
$NICS(1)_{zz}$												

[a] HOMA, $L(d)_{CC}$ and $L(d)_{CC}$ / % are obtained at B3LYP/6–31G(d) level of theory

[b] NICS(1) and $NICS(1)_{zz}$ are obtained at GIAO/HF/6–31G(d)//B3LYP/6–31G(d) level of theory

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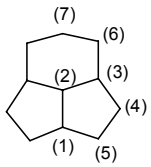
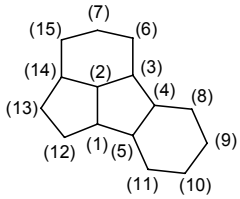
Table S2. Bond distances (in Å),[a] Löwdin π-bond orders (in |e|)[b] (in squared parentheses), Löwdin π-atomic charges (in |e|)[b]. Atom numbering is given below.



1c, 1^-

$1e_{CN}$, 1_{CN}^-



2e, 2^-

$2l_{CN}$, 2_{CN}^-

bond/atom	1c	1^-	2e	2^-	$1e_{CN}$	1_{CN}^-	$2l_{CN}$	2_{CN}^-
C1-C2	1.481	1.390	1.482	1.396	1.474	1.385	1.483	1.395
	[0.15]	[0.55]	[0.17]	[0.53]	[0.17]	[0.53]		[0.51]
C1-C5	1.407	1.447	1.441	1.448	1.407	1.440	1.438	1.436
	[0.54]	[0.49]	[0.40]	[0.44]	[0.53]	[0.48]		[0.45]
C1-C12			1.384	1.437			1.385	1.435
			[0.62]	[0.53]				[0.53]
C2-C3	1.483	1.403	1.485	1.395	1.477	1.394	1.489	1.394
	[0.13]	[0.51]	[0.15]	[0.53]	[0.13]	[0.51]		[0.53]
C2-C14			1.483	1.411			1.475	1.403
			[0.09]	[0.49]				[0.48]
C3-C4	1.411	1.464	1.447	1.475	1.414	1.460	1.452	1.481
	[0.55]	[0.42]	[0.40]	[0.35]	[0.54]	[0.42]		[0.35]
C3-C6	1.395	1.404	1.372	1.400	1.399	1.406	1.378	1.411
	[0.58]	[0.63]	[0.71]	[0.65]	[0.55]	[0.60]		[0.61]
C4-C5	1.423	1.403	1.454	1.469	1.447	1.426	1.452	1.470
	[0.60]	[0.51]	[0.55]	[0.50]	[0.54]	[0.67]		[0.48]
C4–C_4(N)					1.422	1.414		
					[0.26]	[0.34]		
C_4(N)–N					1.163	1.166		
					[0.85]	[0.91]		
C4-C8			1.408	1.391			1.416	1.397
			[0.56]	[0.67]				[0.65]
C5-C11			1.408	1.404			1.412	1.408
			[0.56]	[0.63]				[0.58]
C5–C_5(N)					1.421	1.421		
					[0.25]	[0.30]		
C_5(N)–N					1.163	1.165		
					[0.86]	[0.92]		
C6-C7	1.416	1.418	1.442	1.419	1.438	1.436	1.471	1.440
	[0.62]	[0.64]	[0.44]	[0.62]	[0.57]	[0.59]		[0.56]
C6–C_6(N)					1.430	1.431	1.430	1.430
					[0.26]	[0.30]		[0.29]
C_6(N)–N					1.163	1.163	1.163	1.163
					[0.87]	[0.92]		[0.90]

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bond/atom	1a	$1a^-$	2a	$2a^-$	$1a_{CN}$	$1a_{CN}^-$	$2a_{CN}$	$2a_{CN}^-$
C7-C15			1.393	1.414			1.408	1.428
			[0.76]	[0.66]				[0.60]
C7–C_7(N)					1.430	1.431	1.429	1.432
					[0.29]	[0.31]		[0.30]
C_7(N)–N					1.163	1.164	1.163	1.164
					[0.91]	[0.92]		[0.92]
C8-C9			1.386	1.404			1.409	1.426
			[0.69]	[0.63]				[0.55]
C8–C_8(N)							1.430	1.432
								[0.28]
C_8(N)–N							1.163	1.162
								[0.90]
C9-C10			1.413	1.401			1.422	1.409
			[0.58]	[0.65]				[0.61]
C9–C_9(N)							1.430	1.428
								[0.30]
C_9(N)–N							1.162	1.164
								[0.92]
C10-C11				1.399			1.406	1.414
				[0.66]				[0.58]
C10–C_{10}(N)			1.386				1.430	1.432
			[0.69]					[0.29]
C_{10}(N)–N							1.162	1.163
								[0.93]
C11–C_{11}(N)							1.429	1.429
								[0.30]
C_{11}(N)–N							1.163	1.163
								[0.92]
C12-C13			1.448	1.409			1.473	1.430
			[0.43]	[0.74]				[0.64]
C12–C_{12}(N)							1.423	1.421
								[0.30]
C_{12}(N)–N							1.163	1.164
								[0.92]
C13-C14			1.391	1.451			1.389	1.443
			[0.64]	[0.47]				[0.46]
C13–C_{13}(N)							1.421	1.416
								[0.33]
C_{13}(N)–N							1.163	1.166
								[0.91]
C14-C15			1.418	1.407			1.422	1.405
			[0.41]	[0.61]				[0.58]
C15–C_{15}(N)							1.429	1.432
								[0.29]
C_{15}(N)–N							1.163	1.163
								[0.93]

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bond/atom	1a	$1a^-$	2a	$2a^-$	$1a_{CN}$	$1a_{CN}^-$	$2a_{CN}$	$2a_{CN}^-$
C1	0.97	1.17	0.97	1.19	0.95	1.12		1.15
C2	1.06	1.05	1.03	1.00	1.08	1.03		0.98
C3	0.93	0.98	0.93	1.00	0.91	0.95		0.98
C4	1.01	1.19	0.98	1.01	0.99	1.14		0.99
C_4(N)					0.93	0.89		
N_4					1.05	1.13		
C5	0.97	0.99	0.95	0.91	0.95	0.95		0.89
C_5(N)					0.93	0.91		
N_5					1.04	1.07		
C6	1.03	1.04	1.04	1.04	1.02	1.01		1.02
C_6(N)					0.92	0.90		0.91
N_6					1.06	1.08		1.08
C7	0.97	1.04	0.97	1.09	0.95	1.05		1.05
C_7(N)					0.93	0.90		0.90
N_7					1.03	1.09		1.09
C8			0.97	1.00				0.98
C_8(N)								0.92
N_8								1.06
C9			0.99	1.10				1.06
C_9(N)								0.90
N_9								1.09
C10			0.97	1.01				0.97
C_{10}(N)								0.91
N_{10}								1.06
C11			0.99	1.07				1.05
C_{11}(N)								0.91
N_{11}								1.08
C12			0.99	1.00				0.96
C_{12}(N)								0.91
N_{12}								1.06
C13			1.02	1.20				1.14
C_{13}(N)								0.89
N_{13}								1.13
C14			0.94	1.00				0.97
C15			1.02	1.02				0.99
C_{15}(N)								0.91
N_{15}								1.06

[a] obtained by the B3LYP/6–31G(d) method

[b] obtained by the HF/6–31G(d)//B3LYP/6–31G(d) method