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

Robert Vianello[*a] and Zvonimir B. Maksić[ab]**

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The spatial structure and acidic properties of demethylated Rees hydrocarbons and related fluoradene, as well as their polycyanated derivatives, are considered by the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) method. The molecular frameworks **1c**, **2e** and **3g** involve the π-networks possessing 10, 14 and 18 π-electrons on the molecular rims, held in the rigid tricyclic structures by the central tertiary C(sp^3) carbon atom. It is found that **1c** is a tricyclic [10]annulene with almost uniformly delocalized π-electrons over the molecular perimeter, whereas other systems with 14 and 18 π-electrons exhibit pronounced bond alternation. It is conclusively shown that extended π-electron networks, like *e.g.* that in **3g** include also smaller π-electron patterns conforming to Hückel's ($4n + 2$) rule, thus representing an interesting case of molecular "philogenesis". Further, all these molecules undergo prototropic tautomerism. The number of prototropic tautomers is considerably increased by polycyanation *inter alia* by forming keteneimine moiety. The most important result of the present study is that polycyano derivatives of studied molecules are strong organic Brønsted acids both in the gas-phase (GP) and DMSO. More specifically, percyano molecules **1a$_{\mathbf{CN}}$**, **2a$_{\mathbf{CN}}$** and **3a$_{\mathbf{CN}}$** possess gas-phase ΔH_{acid} values as low as 261.8, 259.0 and 246.3 kcal mol^{-1}, respectively. If the thresholds of superacidity and hyperacidity are accepted as $\Delta H_{\text{acid}}(\text{HClO}_4) = 300.0$ kcal mol^{-1} and the protonation energy of 1,8-bis(dimethylamino)naphthalene DMAN, PA(DMAN) = 245.3 kcal mol^{-1}, respectively, then **1a$_{\mathbf{CN}}$** and **2a$_{\mathbf{CN}}$** are NH superacids, whereas **3a$_{\mathbf{CN}}$** is a C(sp^3)H hyperacid. The origin of the dramatic amplification of the acidity in multiply cyanated derivatives is identified as the increase in the anionic resonance of the resulting conjugate bases.

Introduction

The proton transfer reactions play pivotal role in chemistry, biochemistry and molecular biology. It is, therefore, of utmost importance to gather a wide knowledge and understanding of both Brønsted acidity and basicity of organic and inorganic compounds. This explains the fact that these two fundamental properties were at the focus of intensive interest and investigations of a large number of experimental researchers and theoreticians in the last decade.[1–8] As to the interpretation of the proton affinities of neutral bases and anions, a simple, transparent and intuitively appealing trichotomy formula was put forward recently,[9,10] which proved very useful in this respect[11] as reviewed recently.[12] It should be strongly pointed out that a considerable attention has been devoted to design of powerful neutral organic superacids. This is not surprising because strong organic acids possess some distinct advantages over their mineral counterparts in solutions, since they are reactive in mild chemical environments being central in general acid catalysis.[13,14] In addition, very stable anions derived from superacids are useful in olefin polymerization[15] and in the capture and stabilization of the highly reactive short lived cations such as $\text{HC}_{60}{}^{+}$ and $\text{C}_{60}{}^{\bullet+}$,[16] $\text{C}_6\text{H}_7{}^{+}$ [17] and Bu_3Sn^{+}.[18] Two strategies have been developed for this purpose. The first was based on the application of the electronic super-acceptor substituents,[19,20] whereas the second approach was rooted in the concept of stabilization of the conjugate bases *via* a very strong anionic resonance assisted by a large number of cyano substituents.[21–27] A particularly interesting class of very strong acids is given by carboranes discussed *in extenso* by Reed and co-workers.[16,17,28,29]

Obviously, it is desirable to obtain new superacids, which will enable production of additional highly elusive cations, their stabilization, trapping and experimental characterization. Moreover, a dense ladder of superacids, which enter the domain of strong superbases[30–33] is strongly needed, since their interaction would lead to a spontaneous proton transfer reactions[34,35] and formation of new ion pairs[36,37] offering novel molecular systems exhibiting unexpected, interesting and potentially useful features.

Our starting point for the present analysis have been already synthesized and well studied hydrocarbons,[21–25] which provide

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[a] *Quantum Organic Chemistry Group, Division of Organic Chemistry and Biochemistry, Ruđer Bošković Institute, P.O.Box 180, HR–10 002 Zagreb, Croatia. E-mail: vianello@spider.irb.hr; Fax: (+385) 1-456-1118*
[b] *Faculty of Science, University of Zagreb, Marulićev trg 19, HR–10 000 Zagreb, Croatia*

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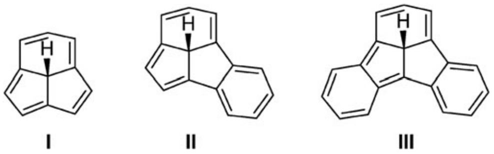


Scheme 1

molecular backbones to be dressed by a large number of electron withdrawing CN groups. The latter substituent was chosen after a detailed study, which revealed that it embodied the optimal compromise between strong electron withdrawing power and very modest steric requirements.[27] This approach is in our view very promising, because the chemistry of the cyano group is known.[38–41] Continuing our efforts in this direction, we consider here Rees hydrocarbons,[42–49] deprived of the methyl group substituted at the central carbon atom (**I–II**) and a related fluoradene tautomer (**III**), which is not prepared as yet (Scheme 1). They will serve as molecular frameworks for powerful neutral organic superacids obtained after polycyanation. Preliminary results on compounds **I** and **II** and their polycyano derivatives were reported earlier.[50] A salient structural feature of these tricyclic compounds is the central bridging C(sp^3)–H subunit, which brings rigidity into the systems, thus "freezing" the annulene network of the π-bonds formed along the molecular perimeter. It will appear that neither of three prototropic tautomers **I**, **II** and **III** belongs to the most stable structure, although they are minima on the potential energy hypersurface (PES). Nevertheless, the [10]annulene character of **I** will be discussed at great length, since it is interesting on its own. Acidity of their polycyanated tautomers will be examined in the gas-phase and DMSO by the modern DFT methods.

Theoretical methodology

Brønsted gas-phase acidity is defined as the negative value of the change in Gibbs free-energy ΔG_{acid} for the proton dissociation reaction:

$$\mathrm{AH\,(g)} \rightarrow \mathrm{A^-\,(g)} + \mathrm{H^+\,(g)} \qquad (1)$$

However, a very good measure of acidity is provided by the negative enthalpy change of the same reaction ΔH_{acid}(AH), which gives the deprotonation energy (DPE), or alternatively absolute proton affinity [APA(A$^-$)] of the corresponding conjugate base A$^-$, which is calculated according to eqn (2):

$$\Delta H_{\mathrm{acid}} = \Delta E_{\mathrm{acid}} + \Delta(PV) \qquad (2)$$

Here ΔE_{acid} is the change in the total molecular energies of the species appearing in eqn (1). It includes the total electronic energy and repulsion of the nuclei, the zero-point vibrational energy (ZPVE) and the finite (room) temperature correction. The pressure–volume work contribution is denoted by $\Delta(PV)$ as usual. It is useful to keep in mind that stronger acids have lower numerical ΔH_{acid} (alias APA(A$^-$) values), which means an easier release of the acidic proton. We shall discuss acidities by considering APA(A$^-$) values keeping in mind that true acidity includes the entropy contribution in the ΔG_{acid} expression, which is given for the sake of completeness.

The theoretical method of choice should be the best compromise between feasibility and practicality on one side and reliability and accuracy on the other. This is the reason why we selected DFT-B3LYP method[51,52] as an appropriate approach for large molecules. It is efficient and inexpensive in terms of the computer time and yet it gives results with a satisfactory accuracy.[7,8,21–25] This is not surprising, because the applied B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) scheme employs a large basis set in the final single–point calculations, capable to offer a good description of resulting anions, whereas the molecular geometries are optimized at a very economical B3LYP/6-31G(d) level. The use of a more flexible basis set for geometry optimization did not significantly affect the final results in several test cases. It is also noteworthy that Pople's triple-zeta basis sets including the polarization and diffuse functions yield practically converged energies for the DFT–B3LYP approach.[53] The adopted approach is also corroborated by extensive calculations of Schaefer III and co-workers,[54–58] which gave a good accordance with experiment for the electron affinities of atoms and molecules. The results of the acidity calculations of Merrill and Kass[59] and Koppel and co-workers[60] also support this contention. This and other evidence lend credence to the results presented here, which put new organic superacids on the (theoretical) acidity ladder established earlier.[21–25]

Taking into account published data, it is safe to conclude that the high level *ab initio* and DFT methods predict basicity and acidity of molecules quite accurately in the gas-phase.[7–8,61] The problem is much more complex in solutions.[62] Whilst an accurate first-principle CBS-QB3 method based on the polarized conductor model can be applied in small molecules with the root-mean-square error lower than 0.4 pK_a units,[63,64] in larger systems one has to resort to more approximate schemes. Fortunately, this is possible with a relatively small sacrifice in accuracy. One can use the isodensity polarized continuum model (IPCM)[65,66] in conjunction with the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) method and consider the proton transfer reaction between a solute and solvent (dimethyl sulfoxide, Me$_2$SO) molecule:

$$\mathrm{AH} + \mathrm{Me_2SO} \rightarrow \mathrm{A^-} + \mathrm{Me_2SOH^+} + \Delta_r H_{\mathrm{DMSO}} \qquad (3)$$

The cavity embracing the solute molecule AH is defined by the molecular surface with constant density of 0.0004 e B^{-3} as proposed by Wiberg and co-workers.[67,68] Extensive calculations and comparison with the measured data gave a good correlation for a wide variety of neutral C–H acids:

$$\mathrm{p}K_a(\mathrm{theor}) = 0.661\Delta_r H_{\mathrm{DMSO}} - 7.7 \qquad (4)$$

as evidenced by an average absolute error of 1.1 pK_a units and a high correlativity coefficient (R^2 = 0.985).[69] This accuracy is sufficient for our aims.

All calculations were carried out with the GAUSSIAN 98 program package.[70]

Results and discussion

7b*H*-cyclopenta[*cd*]indenes I

It is well known for some time that the monocyclic [10]annulene is a floppy molecule, which is highly distorted and nonplanar,[71,72] thus devoiding aromatic character to considerable extent. The most recent high level calculations convincingly show that [10]annulene cannot assume a planar structure of the D_{10h} symmetry due to ring strain, but adopts the non-aromatic C_2 twist form instead.[73–75] In contrast, Rees hydrocarbons possess a somewhat deformed central tetrahedral C(sp^3) carbon atom (substituted by the CH_3 group), which brings rigidity into the system and still enables an appreciable π-electron conjugation over the molecular perimeter due to significant overlapping of the atomic $2p_\pi$ orbitals.[42–44,46] Thus a [10]annulene π-electron network is formed on the peripheral C–C bonds in the most characteristic structure **I** yielding an almost uniform distribution of the *d*(CC) bond distances over the molecular rim (*vide infra*). We shall consider unprotected 7b*H*-cyclopenta[*cd*]indene and its seven-fold cyano derivatives in great detail, since their essential features are shared by other systems described here. Consequently, the latter will be discussed in a more condensed form.

The most stable hydrocarbon tautomer **1a** and its prototropic tautomers **1b–1g** are depicted in Fig. 1. They are all true minima on the PES.

The relative energies against the molecule **1a** are given by the B3LYP/6-31G(d) method, since these relative values are in very good agreement with the single–point B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) energies as a rule with a very few exceptions (*vide infra*). The more accurate single-point calculations will be utilized in many important cases too. It follows that **1a** and **1b** are the most stable species as expected, because they contain a planar benzene moiety. In contrast, **1d–1f** do not involve a benzene fragment and consequently are less stable. It is interesting to point out that the difference in energy between **1a** and **1d** is about 23 kcal mol^{-1}, which corresponds to the aromatic stabilization of the six-membered ring in this particular chemical environment, compared to the conjugation of the alternating single and double bonds in **1d**.

The most acidic proton belongs to the C(sp^3)–H bond in all tautomers. The ΔH_{acid} values for **1a**, **1b** and **1c** are 345.6, 336.3 and 331.0 kcal mol^{-1}, respectively, which means that they are moderately acidic molecules (Table 1).

It is important to point out that the resulting anion (conjugate base) is the same in all three cases. It has a planar framework stabilized by the anionic resonance as illustrated by Scheme 2, where all resonance structures possess an additional mirror image π-electron pairing scheme, except the first and the last one, thus resulting in 15 resonance structures in total. Notice that benzene moiety possesses two Kekulé structures.

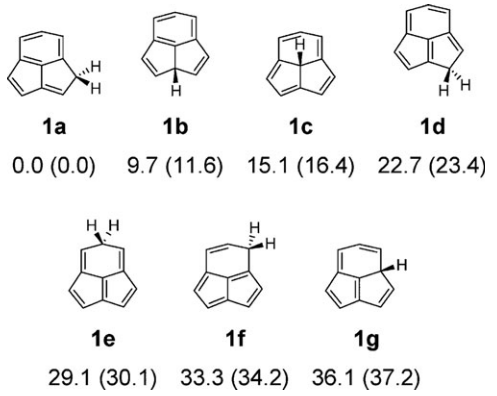


Fig. 1 Schematic representation of 7b*H*-cyclopenta[*cd*]indene tautomers and their relative energies obtained by the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) and B3LYP/6-31G(d) models. The latter are given within parentheses (in kcal mol^{-1}).

It should be stressed that the anionic resonance is strong despite the antiaromatic number of the 12π-electrons. Since all tautomers **1a–1g** share the same final conjugate base, the variations in their acidity is determined by their ground state (GS) energies. In other words, their acidity changes are a consequence of the initial state properties. This conclusion is general and holds for each family of molecules examined in this report. It should be pointed out that **1a** is the least acidic compound in the family of **1a–1g** tautomers. Therefore, one can say that **1a** system provides the upper bound for the ΔH_{acid} values and a lower bound for acidity, where the term bound means borderline or limit, which cannot be surpassed.

The seven-fold CN substitution leads to 11 prototropic tautomers (Fig. S1, ESI†).

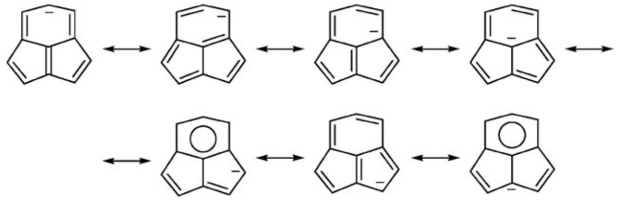
It is important to point out that we shall consider in general the salient features of the most stable four cyano tautomers **1a$_{\text{CN}}$**, **1b$_{\text{CN}}$**, **1c$_{\text{CN}}$** and **1d$_{\text{CN}}$** and the system like **1e$_{\text{CN}}$** here, which corresponds to synthesized hydrocarbon methyl derivative (Fig. 2). The remainder of the data are deposited as ESI.† It should be noted that in polycyanated 7b*H*-cyclopenta[*cd*]indenes **1a$_{\text{CN}}$–1k$_{\text{CN}}$** (Fig. 2 and Fig. S1, ESI†) the simple B3LYP/6-31G(d) scheme reproduces the relative stability of tautomers rather well. Further, it is noteworthy that the most stable structures **1a$_{\text{CN}}$**, **1b$_{\text{CN}}$** and **1c$_{\text{CN}}$** possess a benzene moiety as a stabilizing factor as intuitively expected. Another characteristic feature of multiply substituted cyano derivatives is formation of the keteneimine $C{=}C{=}NH$ group. One of these tautomers exhibits the largest stability, an important reason being extension of the π-network (a notable exception being **3a$_{\text{CN}}$** system, see later). Comparison of the total molecular energies between **1a$_{\text{CN}}$** and **1d$_{\text{CN}}$** indicates that semi-isolated benzene moiety in the former molecule contributes 12 kcal mol^{-1} to the enhanced stability. The C(sp^3) centers in **1b$_{\text{CN}}$** and **1c$_{\text{CN}}$** decrease stability relative to **1a$_{\text{CN}}$** by 2.5 and 7.9 kcal mol^{-1}, respectively. This is intuitively clear too, since the non-planarity in **1c$_{\text{CN}}$** is more pronounced compared to **1b$_{\text{CN}}$**. It is noteworthy that both **1a$_{\text{CN}}$** and **1b$_{\text{CN}}$** are derivatives of **1a**, the keteneimine species being more favorable. Finally, the suspected [10]annulene structure **1e$_{\text{CN}}$** is the fifth most stable structure with a diminished stability by 15 kcal mol^{-1} (Fig. 2). Deprotonation of all tautomers **1a$_{\text{CN}}$–1k$_{\text{CN}}$** yields a single conjugate base, which should be very stable, because the strong resonance effect occurring in the parent hydrocarbon (Scheme 2) is additionally amplified by the π-electron interaction between carbon atoms of the framework and the CN groups, thus giving rise to a $C{=}C{=}N^-$ distribution of the π-density. In other words, the cyano groups enable a considerably better accommodation (dispersion) of the negative charge in the anion. This is in line with the detailed study of the charge migration analysis of the bonded $-C{\equiv}N$ group performed by Clementi.[76] It comes, therefore, as no surprise that the acidity of cyanated compounds is appreciably amplified in spite of the antiaromatic number of the π-electrons in the π-network of the corresponding conjugate base. The ΔH_{acid} values for **1a$_{\text{CN}}$**, **1b$_{\text{CN}}$**, **1c$_{\text{CN}}$**, **1d$_{\text{CN}}$**, **1e$_{\text{CN}}$** are 261.8, 259.1, 253.9, 250.3 and 246.9 kcal mol^{-1}, respectively. It is of interest to put these

Table 1 Total molecular energies of the studied molecules in the gas phase (GP) and in dimethyl sulfoxide (DMSO) obtained at the B3LYP/6-311 + G(2d,p)//B3LYP/6-31G(d) level of theory. H_{corr} denotes thermal correction to enthalpy obtained by the B3LYP/6-31G(d) model. Theoretical pK_a values are obtained using eqn (4)

Molecule	$E_{\mathrm{GP}}{}^{a}$	$H_{\mathrm{corr}}{}^{a}$	$G_{\mathrm{corr}}{}^{a}$	$\Delta H_{\mathrm{acid}}{}^{b}$	$\Delta G_{\mathrm{acid}}{}^{b}$	$\Delta_r H_{\mathrm{DMSO}}{}^{b}$	pK_a(theor)^{c}
1a	−424.04913	0.16115	0.12120	345.6	337.9	38.9	18.0
1b	−424.03362	0.16060	0.12101	336.3	328.3	28.4	11.1
1c	−424.02507	0.16028	0.12081	331.0	323.0	23.6	7.9
$\mathbf{1}^{-}$	−423.48597	0.14648	0.10653				
$\mathbf{1a}_{\mathbf{CN}}$	−1069.86928	0.16205	0.09024	261.8	254.6	−22.5	−22.6
$\mathbf{1b}_{\mathbf{CN}}$	−1069.86540	0.16263	0.09051	259.1	252.0	−22.5	−22.6
$\mathbf{1c}_{\mathbf{CN}}$	−1069.85681	0.16221	0.09066	253.9	246.5	−26.4	−25.2
$\mathbf{1d}_{\mathbf{CN}}$	−1069.85020	0.16147	0.08924	250.3	243.3	−31.2	−28.3
$\mathbf{1e}_{\mathbf{CN}}$	−1069.84513	0.16163	0.09009	246.9	239.5	−19.3	−20.5
$\mathbf{1}_{\mathbf{CN}}{}^{-}$	−1069.44273	0.15045	0.07945				
2a	−577.74952	0.21104	0.16502	341.3	334.0	33.7	14.6
2e	−577.71084	0.20993	0.16419	317.8	310.2	10.9	−0.5
$\mathbf{2}^{-}$	−577.19310	0.19654	0.15081				
$\mathbf{2e}_{\mathbf{CN}}$	−1408.06786	0.21156	0.12459	259.0	251.9	−13.7	−16.8
$\mathbf{2l}_{\mathbf{CN}}$	−1408.03216	0.21110	0.12501	236.9	229.2	−34.4	−30.4
$\mathbf{2}_{\mathbf{CN}}{}^{-}$	−1407.64560	0.19999	0.11376				
3a	−731.43399	0.26068	0.20876	330.3	322.8	27.0	10.1^{d}
3g	−731.38968	0.25916	0.20718	303.5	296.0	0.7	−7.2
$\mathbf{3}^{-}$	−730.89552	0.24644	0.19468				
$\mathbf{3a}_{\mathbf{CN}}$	−1746.24185	0.26129	0.16074	246.3	239.1	−21.1	−21.6
$\mathbf{3m}_{\mathbf{CN}}$	−1746.20130	0.25993	0.15956	221.7	214.4	−45.5	−37.8
$\mathbf{3q}_{\mathbf{CN}}$	−1746.19116	0.26059	0.15883	215.0	208.5	−57.9	−46.0
$\mathbf{3}_{\mathbf{CN}}{}^{-}$	−1745.83952	0.24928	0.14952				

[a] In a.u. [b] In kcal mol^{-1}. [c] In pK_a units. [d] Experimental value is 10.5 (taken from ref. 96).

results into perspective by comparison with very strong Brønsted mineral acids. It should be recalled that Gillespie and Peel[77] defined superacids as substances stronger in acidity than 100% sulfuric acid. Although this definition holds in solutions, it is useful to give here the experimental gas-phase ΔH_{acid} values of HNO_3, H_2SO_4 and $HClO_4$, which are 324.5, 306.3 and 288.0 kcal mol^{-1}, respectively, for comparison.[78] It follows that $\mathbf{1a}_{\mathbf{CN}}$, $\mathbf{1b}_{\mathbf{CN}}$, $\mathbf{1c}_{\mathbf{CN}}$, $\mathbf{1d}_{\mathbf{CN}}$ and $\mathbf{1e}_{\mathbf{CN}}$ are stronger acids than H_2SO_4 (in the gas-phase) by some 32, 34, 38, 41 and 43 orders of magnitude, in the same order, which is a remarkable finding indeed. Another operational definition of the superacidity threshold, which would be perhaps more practical in the gas-phase, should be the deprotonation enthalpy of $HClO_4$, which is 300 kcal mol^{-1}.[79] If this criterion is accepted, then the most stable cyano system $\mathbf{1a}_{\mathbf{CN}}$ is by 28 orders of magnitude more acidic than the threshold of superacidity. It should be kept in mind that it is the NH acid. By the same token, we would like to suggest that the gas-phase proton affinity of the first proton sponge 1,8-bis(dimethylamino)-naphthalene, DMAN (245.3 kcal mol^{-1})[78] is the threshold of hyperstrong acidity, since it is widely accepted lower bound for superbasicity. A variation in acidity of polycyanated compounds $\mathbf{1a}_{\mathbf{CN}}$–$\mathbf{1k}_{\mathbf{CN}}$ is given by the initial state properties as mentioned earlier. In contrast, a dramatic increase in acidity between the parent hydrocarbons **1a**, **1b** and **1c** upon sevenfold cyanation (as in $\mathbf{1b}_{\mathbf{CN}}$, $\mathbf{1c}_{\mathbf{CN}}$ and $\mathbf{1e}_{\mathbf{CN}}$) is as large as 86.5, 82.4 and 84.1 kcal mol^{-1}, respectively, which is predominantly a consequence of a difference in their final states.



Scheme 2

9c*H*-cyclopenta[*jk*]fluorenes II

9c*H*-cyclopenta[*jk*]fluorene is obtained by annelation of the benzene ring to the parent compound **I**. It has altogether 15 prototropic tautomers (Fig. S2, ESI†). The most stable ones are presented in Fig. 3.

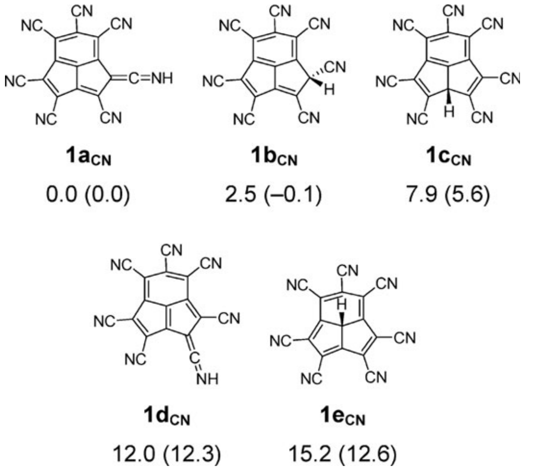


Fig. 2 Prototropic tautomerism in heptacyano-7b*H*-cyclopenta-[*cd*]indene. The relative stabilities (in kcal mol^{-1}) are calculated by the B3LYP/6-311 + G(2d,p)//B3LYP/6-31G(d) and (B3LYP/6-31G(d)) methods.

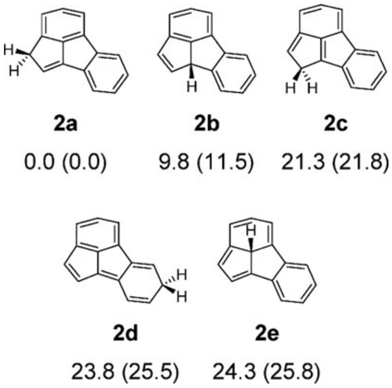


Fig. 3 Schematic representation of 9c*H*-cyclopenta[*jk*]fluorene tautomers and their relative energies obtained by the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) and B3LYP/6-31G(d) models. The latter are given within parentheses (in kcal mol^{-1}).

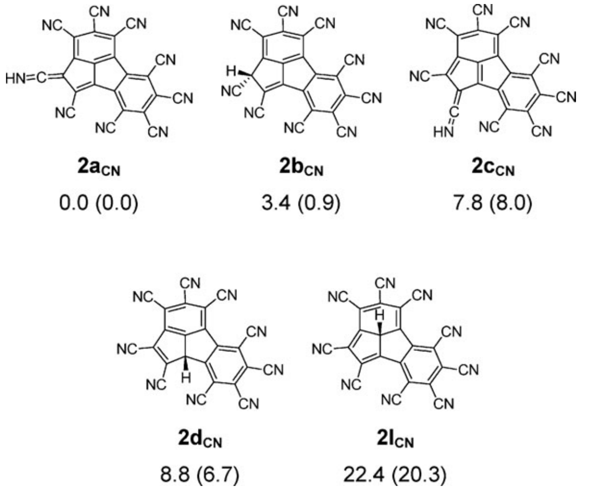


Fig. 4 Prototropic tautomerism in nonacyano-9c*H*-cyclopenta-[*jk*]fluorene. The relative stabilities (in kcal mol^{-1}) are calculated by the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) and (B3LYP/6-31G(d)) methods.

The synthesized molecule is 9c*H*-methyl derivative,[47] which corresponds to tautomer **2e** substituted by the CH$_3$ group at the central carbon. The latter is the fifth most stable compound. The system **2d** is practically degenerate in energy with **2e**, although it is widely different in its spatial and electronic structure. Interestingly, both tautomers **2d** and **2e** possess a benzene fragment, which undoubtedly contributes to their stability. The same holds for the system **2c**, which is more stable by 3 kcal mol^{-1}. However, two most stable tautomers **2a** and **2b** include two separated benzene fragments. The latter is higher in energy relative to **2a** by 9.8 kcal mol^{-1}, however, because of the nonplanarity induced by the tertiary C(sp^3) atom. Tautomer **2a** yields acidity, which is the upper bound for the ΔH_{acid} values (341.3 kcal mol^{-1}). It is relatively high, but still lower by 4 kcal mol^{-1} than ΔH_{acid}(**1a**). This is a consequence of the fact that larger π-networks can accommodate the negative charge better than smaller systems, in accordance with a general behavior of the extended π-system. One should reiterate that the antiaromatic number of 16π electrons does not preclude a strong anionic resonance in $\mathbf{2}^-$.

The nona-cyano derivatives form a large family of 24 prototropic tautomers in total (Fig. S3, ESI†). The first four and the paradigmatic system $\mathbf{2l_{CN}}$ are shown in Fig. 4.

Tautomer including keteneimine moiety $\mathbf{2a_{CN}}$ is the most stable molecule thus being the NH acid. Both $\mathbf{2a_{CN}}$ and $\mathbf{2b_{CN}}$ are derivatives of the most stable pure hydrocarbon **2a**. Acidities of $\mathbf{2a_{CN}}$ and $\mathbf{2l_{CN}}$ are 259.0 and 236.9 kcal mol^{-1}, respectively, the former value being the upper bound for the ΔH_{acid} values for this family of compounds. The corresponding increase in acidity upon nine-fold cyanation of the parent hydrocarbons **2a** and **2e** is 82.3 and 80.9 kcal mol^{-1}, respectively. Hence, one can conclude that the amplification of acidity induced by the nine-fold cyanation is comparable to that found in heptacyano derivatives of 7b*H*-cyclopenta-[*cd*]indene being in the range of 81–87 kcal mol^{-1}, which implies that the increase is fairly constant.

Fluoradene III

Fluoradenes are best represented by the archetypal tautomer **3a**, which was synthesized some thirty years ago[80] giving the name to the whole family (Fig. 5). A complete list of all 11 fluoradenes is given in Fig. S4, ESI.† It is obtained by simple extension of 9c*H*-cyclopenta[*jk*]fluorene tautomer **2b** by fusion of a new six-membered benzene ring thus forming the left wing.

The pronounced stability of **3a** is a consequence of the three almost isolated benzene rings. It is interesting to notice that **3a** is more stable than **3g** by 28 kcal mol^{-1}, due to additional benzene ring, which is comparable to the aromatic stabilization deduced from comparison of the planar tautomers **1a** and **1d** (23 kcal mol^{-1}) and a value of 24 kcal mol^{-1} obtained by a difference in energies between **2a** and **2d**. Seven out of 11 tautomers possess two aromatic benzene rings. The heavy atoms are planar in **3b**, **3c** and **3d**. On the other hand, molecule **3g** has the tertiary C(sp^3) center thus being nonplanar and potentially possesses [18]annulene periphery. However, this is not the case, as revealed by the dominant resonance structures. One of them is depicted in Fig. 5, whereas the other is obtained by its mirror image. As a consequence, the [18]annulene

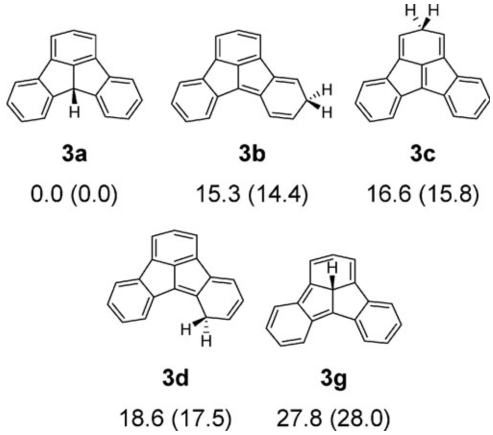


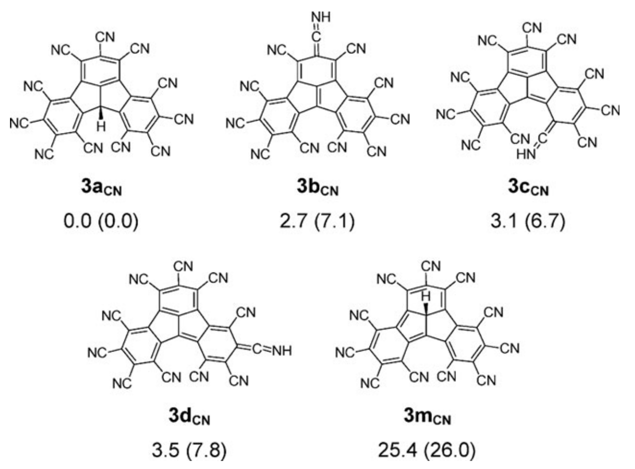
Fig. 5 Schematic representation of fluoradene tautomers and their relative energies obtained by the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) and B3LYP/6-31G(d) models. The latter are given within parentheses (in kcal mol^{-1}).

pattern can not be formed, because of the competition with the aromatic sextet of the flanked benzenes. However, the most striking was the finding that other π-electron patterns already encountered in **1b** and **2b** also participate in the competition in a significant extent (*vide infra*).

Deprotonation of tautomers **3a–3k** yields a planar 20π-electron network, which is formally antiaromatic by the electron count rule. In spite of that it should exhibit substantial anionic resonance leading to delocalization of the excess electron density. This is indeed the case as evidenced by the ΔH_{acid} values of **3a** and **3g**, which assume 330.3 and 303.5 kcal mol^{-1}, respectively. It follows that the system **3g** would provide a very strong organic acid, if once synthesized. This depends, however, on the barrier height for the H-transfer from the central carbon atom in **3g** to the peripheral C(sp^3) carbon in **3a**.

The eleven-fold cyanation leads to 17 prototropic tautomers (Fig. S5, ESI†). The most stable four ones are depicted in Fig. 6 as well as **3m$_{\mathbf{CN}}$**, which belongs to the least stable undecacyano-fluoradene tautomers.

The most stable cyano derivative **3a$_{\mathbf{CN}}$** corresponds to the undeca-substituted synthesized fluoradene **3a**. The fact that the most stable tautomer is not keteneimine compound is a consequence of the structural characteristics, which render impossible formation of the keteneimine fragment. Thus **3a$_{\mathbf{CN}}$** is lower in energy than the most stable keteneimine system **3b$_{\mathbf{CN}}$** by 2.7 kcal mol^{-1}. The enhancement of acidity leads to the record holding superacid, since ΔH_{acid}(**3a$_{\mathbf{CN}}$**) assumes 246.3 kcal mol^{-1}. This value comes very close to the borderline of hyperacidity (245.3 kcal mol^{-1}). It is probably not exaggerated to say that **3a$_{\mathbf{CN}}$** represents the first neutral organic hyperacid. On the other hand, we note in passing that **3m$_{\mathbf{CN}}$** would have, if synthesized, ΔH_{acid} = 221.7 kcal mol^{-1}, which would represent the record holding hyperacidic system. The corresponding increase in acidity upon cyanation is 84.0 and 81.8 kcal mol^{-1}, which lies within the range discussed earlier. The reason why **3a$_{\mathbf{CN}}$** is a hyperstrong neutral acid is given by the fact that the acidity of the unsubstituted hydrocarbon **3a** is already high. Since fluoradene **3a** is already prepared, its polycyanation would provide one of the most powerful organic superacids predicted so far by theoretical methods *in silico*. Superacids **3a$_{\mathbf{CN}}$** and **3m$_{\mathbf{CN}}$** are by 39 and 57 orders of magnitude stronger acids in the gas-phase than the threshold value of $HClO_4$ (300 kcal mol^{-1}).



3a$_{\mathbf{CN}}$ 0.0 (0.0)

3b$_{\mathbf{CN}}$ 2.7 (7.1)

3c$_{\mathbf{CN}}$ 3.1 (6.7)

3d$_{\mathbf{CN}}$ 3.5 (7.8)

3m$_{\mathbf{CN}}$ 25.4 (26.0)

Fig. 6 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.

Structural characteristics, aromaticity indices and charge distribution

Structures and aromaticities. The most striking features of some typical systems deserve to be discussed in more detail. Compounds possessing the bridging C(sp^3) carbon center, like *e.g.* **1c**, **2e** and **3g** are obviously nonplanar. This holds also for the cyano derivatives with and without keteneimine group. Moreover, additional deviations from planarity are caused by the steric congestion of the cyano groups in heavily substituted derivatives in spite of their modest spatial requirements. The C(sp^3) atom is considerably pyramidalized. A degree of pyramidalization of its three CC bonds is conveniently calculated by the formula:[81]

$$\mathrm{DP}(\%) = \frac{\left[360^{\circ} - \sum_{i=1}^{3} \alpha_i^{\circ}\right]}{0.9^{\circ}} \tag{5}$$

where three C–C–C bond angles are given in degrees as well as the normalization factor 0.9. It is noteworthy that the maximum pyramidalization of 100% occurs by definition when the three sharp CCC angles achieve 90°, whereas the perfectly tetrahedral C(sp^3) atom would have DP(%) = 35% if only three CC bonds are considered. It turns out that the C(sp^3) carbon is pyramidalized in **1c**, **2e**, **3g**, **1e$_{\mathbf{CN}}$**, **2e$_{\mathbf{CN}}$** and **3m$_{\mathbf{CN}}$** by 28.0, 27.4, 24.2, 29.6, 29.3 and 24.3%, respectively. In other words, the pyramidalization is relatively high in the systems above and it does not significantly change either in related systems or upon polycyanation. Deprotonation of the C(sp^3)–H center leads to the C(sp^2) rehybridization and contributes to the subsequent planarization of anions, thus enabling optimal anionic resonance. Some nonplanarity induced by the crowded CN groups persists, however.

The differences in bond distances between **1c** and **1**$^-$ are interesting. It should be emphasized that the latter anion is selected in examining the effect of the basis set on the calculated geometries. Three basis sets 6-31G(d), 6-31+G(d) and 6-311+G(d,p) are studied within the B3LYP and MP2 methodologies (Fig. S6, ESI†). It appears that the CC bond lengths do not strongly depend either on the applied method or basis set. More specifically, the average absolute deviations of the B3LYP/6-31G(d) C–C bond distances from the B3LYP/6-31+G(d) and B3LYP/6-311+G(d,p) results are 0.002 and 0.001 Å, respectively. The corresponding deviations for the MP2 calculations by using the same larger basis sets are 0.004 and 0.005 Å. This finding justifies the efficient and economical calculation of geometries of very large systems by B3LYP/6-31G(d) scheme. In particular, the total molecular energies should not be affected at all by small variation in the structural parameters, since they change very slowly near the minima on the potential energy surface.

Inspection of relevant geometrical parameters of neutral **1c** reveals that it represents elusive tricyclic quasi-[10]annulene

(Fig. S7, ESI†). The CC bond lengths of the perimeter vary in a narrow range between 1.395–1.423 Å, which are close to the aromatic bond distances. Thus, they are consistent with the electrophilic activity of **1c**,[44,45] its photoelectron spectra[49] and diatropicity of the NMR hydrogen chemical shifts.[43] The central CC bonds emanating from the C(sp^3) carbon are longer (~1.483 Å), because they are of the C(sp^3)–C(sp^2) type. This distance is by 0.016 Å larger than the single C(sp^2)–C(sp^2) bond distance of 1.467 Å as found by the electron diffraction measurements in 1,3-butadiene.[82] The central bonds do not participate in the π-electron delocalization, because C(sp^3)–H center acts as an "insulator". There are two ways to determine the partial bond fixation and a degree of aromaticity in delocalized cyclic systems. Simple indices of partial bond fixation and π-bond localization are provided by formulae:[83,84]

$$L(d)_{\mathrm{CC}} = \sum_n |d_{\mathrm{CC}}^{(n)} - \bar{d}_{\mathrm{CC}}| \text{ and } \qquad L(\pi)_{\mathrm{CC}} = \sum_n |\pi_{\mathrm{CC}}^{(n)} - \bar{\pi}_{\mathrm{CC}}| \tag{6}$$

where $\bar{d}_{\mathrm{CC}}$ and $\bar{\pi}_{\mathrm{CC}}$ denote the average CC bond distance and the average π-bond order, respectively, and the summation is extended over the CC bonds of the molecular rim. The $L(d)_{\mathrm{CC}}$ index should be preferred over the $L(\pi)_{\mathrm{CC}}$ one, because it reflects the influence of both the σ- and π-electrons. The perfect aromatization implies $L(d)_{\mathrm{CC}} = 0$ and $L(\pi)_{\mathrm{CC}} = 0$ as in benzene. On the other hand, $L(d)_{\mathrm{CC}}$ in the highly localized model system given by cyclohexatriene is 0.36, which corresponds to 100% bond fixation by definition. This value can be used to obtain the $L(d)_{\mathrm{CC}}$ in percents, whose positive values indicate the aromaticity defect. Alternatively, one can employ the harmonic oscillator model of aromaticity (HOMA) developed by Krygowski and co-workers.[85–87] The HOMA index is defined as:

$$\mathrm{HOMA} = 1 - (\alpha/n)\sum_{i=1}^{n} (d(CC)_{\mathrm{opt}} - d(\mathrm{CC})_i)^2 \tag{7}$$

where summation is the same as in eqn (6), while α is a free parameter determined by a requirement that HOMA = 0 for a reference nonaromatic Kekulé structure of benzene (α = 257.7). Here, n is the number of the CC bonds over the molecular perimeter and $d(\mathrm{CC})_{\mathrm{opt}}$ is the optimized CC bond length for an ideal aromatic compound like *e.g.* in D_{6h} benzene, in which case it is 1.388 (in Å) according to the original prescription. It should be noticed that HOMA index is dimensionless magnitude, which is 1 for fully aromatic ring and multiplied by 100 yields aromaticity of a particular ring in percents. Finally, an approximate qualitative index of aromaticity is given by the nucleus independent chemical shift (NICS), which measures diamagnetic shielding in the external magnetic field at a particular point within the molecular volume.[88,89] This point is customarily taken 1 Å over the centre of the examined ring. We shall use both the total NICS(1) values and its component NICS(1)$_{zz}$ perpendicular to the ring. The latter is recommended by Lazzeretti as a better index of aromaticity than NICS itself.[90,91] The NICS indices are calculated by the GIAO/HF/6-31G(d)//B3LYP/6-31G(d) model. The results are displayed in Table S1, ESI† together with the HOMA and $L(d)_{\mathrm{CC}}$ values. The HOMA parameter shows that the aromaticity of the molecular perimeter in **1c** is 84.8%, which is in accordance with the partial bond fixation of only 10.7%. Both criteria support conclusion that **1c** is a quasi-[10]annulene system. Its deprotonation dramatically changes the picture. The dominant aromatic substructure of the **1**$^-$ anion is that of the aromatic sextet of the planar six-membered ring as evidenced by the HOMA value of 88.1%. This detail does not imply that other delocalization patterns are negligible and that the remainder of the π-density is localized in isolated double bonds and/or the π-lone pair. On the contrary, the five-membered rings and the perimeter cycle exhibit significantly delocalized π-"currents" at the same time, as evidenced by their HOMA values of 49.9 and 45.2%, respectively. We are inclined to interpret these numbers as the relative weights of the various π-electron coupling schemes, which would enter the total valence bond wavefunction within the VB method. It is worth noting that the aforementioned π-electron substructures (patterns) obey Hückel's count rule (*vide infra*). The most important component of the conceived total VB function for **1**$^-$ would be that of the aromatic sextet occurring within the benzene fragment, supplemented by three ways of distributing two local double bonds and one π-lone pair over two coalesced five-membered rings (Scheme 2).

The NICS criterion we shall use only in anions, which are either planar or exhibit very small nonplanarities. It appears that NICS(1) and NICS(1)$_{zz}$ for the six-membered ring in **1**$^-$ are comparable to that of a free benzene (given within parentheses) as evidenced by the calculated values −14.5 (−12.8) and −36.0 (−32.2), respectively. In contrast, the five-membered rings have NICS(1) = −6.7 and NICS(1)$_{zz}$ = −11.3, which are much lower in their absolute values than the corresponding values −14.0 and −36.4 in cyclopentadienyl anion $C_5H_5^-$, taken as the archetypal aromatic five-membered ring system. Hence, these two rings are not aromatized, as it was expected in view of the common fused bond. These data are in qualitative agreement with results obtained by structural indices discussed above.

In 9c*H*-cyclopenta[*jk*]fluorene **2e** the HOMA index for the peripheral delocalized π-pattern indicate 71.6% of the aromatic character. Similarly, the bond fixation is rather high (30.7%) implying that **2e** is not a quasi-[14]annulene. This conclusion is corroborated by a significant role of the [10]-annulene π-pattern of 52.7% inherently present in the **2e** π-system as a substructure. Perusal of the bond distances of the **2e** perimeter shows that they vary over the range of 1.384–1.447 Å, which is relatively large too (Fig. S7, ESI†). The HOMA values in deprotonated conjugate base **2**$^-$ are $(61.5\%)_{14}$, $(31.2\%)_{10}$, $(88.3\%)_6^{\mathrm{up}}$, $(68.3\%)_6^{\mathrm{down}}$, $(61.8\%)_5^{\mathrm{left}}$ and $(8.0\%)_5^{\mathrm{right}}$, where subscripts denote the number of the ring carbons and superscripts signify position of the ring in the overall framework (Table S1, ESI†). The upper benzene fragment exhibits the highest aromaticity, to be followed by the lower benzene moiety, the left five-membered ring and the molecular rim encompassing 14 carbon atoms. Interestingly, HOMA of the right five-membered ring indicates lack of the aromatic character as evidenced also with its $L(d)_{\mathrm{CC}}$ value of

0.164. The bond distances confirm this conjecture. Namely, two CC bond distances of the five-membered rings involving the central carbon atom are 1.395/1.396 Å, two lateral CC bonds possess distances of 1.448 and 1.475 Å, whereas the annelated bond with the flanked benzene fragment is of the distance as large as 1.469 Å (Fig. S7, ESI†). The bond alternation is highly pronounced indeed. The lack of a single dominant π-electron pattern in **2e** indicates a larger total bond fixation, which is reflected in $L(d)_{CC}$ value (28.1%) obtained by taking all CC bonds into account. Finally, let us consider tautomer **3g**. Inspection of the π-electron delocalization patterns and the associated HOMA values (Table S1, ESI†), indicates that the highest weight of 81.8% has the π-pathway over the molecular perimeter. This is followed by two equivalent π-patterns encountered in the 9c*H*-cyclopenta[*jk*]fluorene tautomer **2e** involving 14π electrons and possessing the aromatic character of 70.4% each. Finally, it includes the 7b*H*-cyclopenta[*cd*]indene tautomer **1c** π-electron substructure with 10π electrons and the aromaticity index of 49.9%. All these π-bonding patterns compete for the π-electrons and the full picture is obtained by their superposition. This is the reason why **3g** is not a quasi-[18]annulene system. It does not possess a single dominant [18]annulene π-electron resonance structure extended over the perimeter. Deprotonation diminishes the role of the leading π-electron delocalization patterns of **3g**, as usual, and inaugurates powerful influence of all three benzene rings in $\mathbf{3}^-$, the upper one being dominant with the aromatic character of 90.6%. The contribution of the five-membered rings is very modest (16.5%).

To conclude, it is of some interest to compare magnetic indices of aromaticity with the geometric ones for $\mathbf{2}^-$, $\mathbf{2_{CN}}^-$ and $\mathbf{3}^-$. We shall summarize results in a form of diads $[\text{NICS}(1), \text{NICS}(1)_{zz}]_n$, where the subscript n denotes the size of the substructural ring. In $\mathbf{2}^-$ the corresponding diads read: $[-14.3, -35.2]_6^{\text{up}}$, $[-11.0, -25.9]_6^{\text{down}}$, $[-8.8, -17.5]_5^{\text{left}}$ and $[-5.9, -6.8]_5^{\text{right}}$. Considering the benzene pattern first, it appears that both NICS(1) and $\text{NICS}(1)_{zz}$ very well describe a significant decrease in aromaticity in the lower ring compared to the upper benzene moiety, in accordance with the HOMA prediction. The upper six-membered ring should be equally aromatic as its counterpart in $\mathbf{1}^-$, which is in agreement with their HOMA indices. Similarly, the magnetic and HOMA indices indicate a small increase in the aromatic stabilization of the left five-membered ring in $\mathbf{2}^-$ compared to $\mathbf{1}^-$. In contrast, a strong decrease in the delocalization of the right five-membered ring is borne out by HOMA and $\text{NICS}(1)_{zz}$ parameters, but not by the NICS(1), which seems to fail here. Finally, a slight increase in stabilization of the upper benzene ring in $\mathbf{3}^-$ relative to that in $\mathbf{1}^-$ and $\mathbf{2}^-$ is not reproduced either by NICS(1) or $\text{NICS}(1)_{zz}$ values, indicating that analogy between structural and magnetic criteria does not hold always and that it is more qualitative than quantitative. Similarly, the decrease in delocalization of the right five-membered ring relative to that in $\mathbf{1}^-$ is not well described by both magnetic indices.

Points of considerable importance are changes induced by polycyanation. Focusing on the neutral molecules first, it is safe to say that aromaticity of the various rings' π-substructures is significantly diminished as measured by HOMA index (Table S1, ESI†). This is compatible with the resonance effect between the cyano groups and the carbon framework, as easily deduced by Pauling's resonance structures. It leads to some π-electron density drift from the rings to the nitrogen atoms. Consequently, the situation in anions is more complex. All aromatic rings, which are closed by $(4n + 2)\pi$ electrons (including the molecular perimeter pattern and smaller circular π-substructures) possess lower HOMA values in polycyanated anions compared to the corresponding pure hydrocarbon anions like *e.g.* in $\mathbf{2_{CN}}^-$. The five-membered rings are exception. They increase the aromatic character in polycyanated anions in a tendency to form the aromatic sextet by attracting the excess negative charge as much as possible. It is noteworthy that the changes imposed by polycyanation are followed by the changes in the $\text{NICS}(1)_{zz}$ component much better than by the total NICS(1) values (Table S1, ESI†). This finding supports contention of Lazzeretti that the perpendicular zz-component of the NICS(1) tensor describes better the cyclic conjugation of the π-electrons than the average sum of the diagonal elements.[90,91]

Charge distribution

In order to get a better idea on the distribution of atomic charges, we calculated the atomic total densities, π-densities and π-bond orders. For this purpose we used the density partitioning scheme based on the Löwdin symmetrical orthogonalization.[92] The π-electron distributions reflected in the π-bond orders (given in Table S2, ESI†) are in harmony with conclusions derived from the HOMA indices above. The corresponding numbers are placed within a narrow range of 0.4–0.7 (in |e| units) in all π-electron substructures exhibiting pronounced aromatic character. It should be noted that the higher limit occurs more frequently, indicating the presence of the fairly uniform distribution of the π-density over CC bonds close to that in the free benzene. Let us briefly consider the formal atomic charges in neutral acids and their conjugate bases. They are given in a form of diads, where the first number refers to the acid and second to the conjugate base. The characteristic atomic charges in **1c** and $\mathbf{1}^-$ (in |e|) are (Table S2, ESI†): C1 (−0.04, −0.18), C2 (−0.12, −0.08), C3 (0.00, −0.04), C4 (−0.18, −0.30), C5 (−0.15, −0.16), C6 (−0.19, −0.20) and C7 (−0.15, −0.23). It appears that carbon atoms gain some electron density upon deprotonation, albeit sometimes a tiny amount, and secondly, the resulting negative charges are relatively close in magnitude implying that the excess negative charge is highly delocalized and dispersed. The highest concentration of the negative charge in the anion (−0.30) is found at carbon atom C4, which is a consequence of the tendency to increase the negative charge of the five-membered ring(s). It should be mentioned that the positive charge of the hydrogens in $\mathbf{1}^-$ is also slightly diminished. It turns out that the excess charge is very well dispersed over all atoms in $\mathbf{1}^-$. Comparison of atomic charges between **1c** and $\mathbf{1e_{CN}}$ is instructive (Table S2, ESI†): C1 (−0.04, 0.01), C2 (−0.12, −0.12), C3 (0.00, 0.05), C4 (−0.18, 0.02), C5 (−0.15, 0.05), C6 (−0.19, 0.00) and C7 (−0.15, 0.05). Hence, the carbon atoms of the peripheral ring linked to CN groups become practically electro-neutral due to a density shift to the substituents. Other carbon charges are either unchanged or undergo very small changes. For example, the central atom C2 has the negative charge of −0.12 |e|, which is pulled directly from the H atom in **1c** and $\mathbf{1e_{CN}}$, being unaffected by the CN substitution. It is surprising that the electronegative nitrogens of the CN groups carry a small negative charge of only −0.05 |e|, which is counterintuitive. In this connection it is useful to recall that Löwdin's partitioning of the total molecular electron density into atomic contributions probably underestimates the intramolecular charge transfer, in contrast to Mulliken's 50 : 50 criterion, which exaggerates it.[93] The best estimates are probably somewhere in between. However, if we stick with Löwdin partitioning in a consistent way, it is plausible to assume that reasonable trends of changes are obtained, in spite of its approximate nature. One of the very important mechanisms, which increase acidity of neutral acids,[21–27,50] is the anionic resonance occurring in the conjugate bases. This is the final state effect, which should increase the electron density placed on the nitrogen atoms. It is nicely borne out by calculations on $\mathbf{1_{CN}}^-$, since the negative charge of the nitrogen atoms in cyano groups attached to the carbons C4, C5, C6 and C7 are −0.16, −0.13, −0.12 and −0.13 |e|, respectively (Table S2). They are larger in absolute values than those obtained for the neutral acid $\mathbf{1e_{CN}}$. It also appears that the excess negative charge is better dispersed in $\mathbf{1_{CN}}^-$ than in its unsubstituted counterpart $\mathbf{1}^-$, as intuitively expected on the basis of much larger number of the resonance structures in the former conjugate base. The gain in the electron density by the carbons is also an important part of the electron reorganization effect in $\mathbf{1_{CN}}^-$, because they were previously deprived of some of their electron density in $\mathbf{1e_{CN}}$ due to pronounced electronegativity of the nitrogens. This deficit is recovered upon deprotonation as a rule leading to significant stabilization of the anion. It is interesting to point out that the central atom C2 has lower π-electron density in $\mathbf{1_{CN}}^-$ (1.03 |e|) than in the anion of the parent compound $\mathbf{1}^-$ (1.05 |e|), which is consistent with a density transfer to nitrogens. The same takes place in $\mathbf{2_{CN}}^-$ (0.98 |e|) as compared to $\mathbf{2}^-$ (1.00 |e|) and in $\mathbf{3_{CN}}^-$ (0.98 |e|) against $\mathbf{3}^-$ (0.96 |e|). The distribution of the electron density over the molecular perimeters in anions is also indicative of the migration to the CN fragments. For instance, the π-electron population of the carbon atoms on the rim in $\mathbf{1}^-$ and $\mathbf{1_{CN}}^-$ is 10.67 and 10.27 |e|, respectively. The corresponding values in $\mathbf{2}^-$ and $\mathbf{2_{CN}}^-$ are 14.64 *vs.* 14.20 |e|, whereas the results for $\mathbf{3}^-$ and $\mathbf{3_{CN}}^-$ read 18.60 and 18.12 |e|, in the same order. The decrease in the π-density upon cyanation is 0.40, 0.44 and 0.48 |e|, respectively. The bottom line of this discussion is that relatively small changes in the spatial structure and electron distribution triggered by deprotonation profoundly affect the acidity of the polycyano compounds. Conclusions drawn above hold for other molecules studied here.

Triadic analysis of the gas-phase acidity

A useful tool for interpretation of acidities is provided by the triadic formula,[10] which treats deprotonation as a reversed process — protonation of the studied conjugate base A⁻:

$$\mathrm{APA(A^-)_\alpha} = -\mathrm{IE(A^-)}_n^{\mathrm{Koop}} + E(\mathrm{ei})_{\mathrm{rex}}^{(n)} + (\mathrm{BAE})^{\bullet}{}_{\alpha} + 313.6\ \mathrm{kcal\ mol^{-1}} \quad (8)$$

where the site of protonation is denoted by α. *N*-th Koopmans' ionization energy $\mathrm{IE(A^-)}_n^{\mathrm{Koop}}$ of the anion A^- is calculated in the frozen electron density and clamped nuclei approximation (counting the HOMO as the first molecular orbital). Hence, $\mathrm{IE(A^-)}_n^{\mathrm{Koop}}$ mirrors the properties of the final state (conjugate base A^-) in the deprotonation event. The reorganization effect following electron ejection by ionization of the anion is described by the relaxation energy $E(\mathrm{ei})^{(n)}{}_{\mathrm{rex}}$ defined by eqn (9):

$$E(\mathrm{ei})_{\mathrm{rex}}^{(n)} = \mathrm{IE(A^-)}_n^{\mathrm{Koop}} - \mathrm{IE(A^-)}_1^{\mathrm{ad}} \quad (9)$$

Finally, the bond dissociation energy related to the scission of the C–H bonds in the deprotonation process at position α (or alternatively the bond association energy (BAE) in the reversed protonation of the conjugate base) is given by the term $(\mathrm{BAE})^{\bullet}{}_{\alpha}$. The first adiabatic ionization energy of A^- is denoted by $\mathrm{IE(A^-)_1}^{\mathrm{ad}}$. It should be mentioned for the sake of clarity that *n*-th ionization energy $\mathrm{IE(A^-)}_n^{\mathrm{Koop}}$ is related to a specific MO that is most affected by protonation, which is a distinct advantage of the triadic approach. It is usually the (localized or partially localized) MO describing lone pair residing on the atom under proton attack. In delocalized systems it is the MO with highest orbital energy, which has the largest density at the attacked atom. For some representative systems studied here, the PRIMO orbitals are depicted in Fig. S8, ESI.† The triadic analysis applied here is carried out at the B3LYP/6-311 + G(2d,p)//B3LYP/6-31G(d) level of theory, whereas Koopmans' ionization energies are computed by the restricted HF/6-311 + G(2d,p)//B3LYP/6-31G(d) model. Bond dissociation energies are obtained by use of the unrestricted B3LYP/6-311 + G(2d,p)//B3LYP/6-31G(d) approach. Some additional characteristic systems are considered here for illustrative purposes. They encompass cyclopentadiene (**4**), pentacyanocyclopentadiene tautomer with HC(sp^3)–CN functionality (**5**) and its more stable keteneimine tautomer (**6**) involving C═C═NH fragment.

A change in $\mathrm{PA(A^-)_\alpha}$ relative to a predetermined reference molecule is succinctly given by a triad of values:

$$\Delta\mathrm{APA(S_\alpha,R_\beta)} = [\Delta(-\mathrm{IE}_{n\alpha,n\beta}^{\mathrm{Koop}}); \Delta E(\mathrm{ei})_{\mathrm{rex}}^{(n\alpha,n\beta)}; \Delta(\mathrm{BAE})^{\bullet}{}_{n\alpha,n\beta}] \quad (10)$$

where S and R stand for an anion under study and the reference anion, respectively. The difference is taken against the gauge anion R. The squared parentheses imply summation of three terms. All numbers are given in kcal mol⁻¹.

Triadic analysis gives a simple rationalization of the difference in acidity between different sites within the same molecule, then between prototropic tautomers of the same family of molecules and finally, between widely different compounds varying in size and belonging to different families. Let us first address the question why **1c** is more acidic than cyclopentadiene **4**. Eqn (10) offers a straightforward answer: APA(**1c**⁻) − APA(**4**⁻) = [−26.2; 21.4; −18.1] = −22.9 kcal mol⁻¹ (Table 2). It follows that the increased acidity is a combined contribution of the initial and final state effects. The C(sp^3)–H bond energy is smaller in **1c** by 18.1 and the PRIMO orbital is lower in its energy in **1c** by 26.2 kcal mol^{-1}. In contrast, the relaxation effect diminishes acidity of **1a**, since it increases APA(**1c**$^-$). It should be strongly pointed out that the relaxation should not be misunderstood with the anionic resonance stabilization, which increases acidity, since they are different by their very definitions. Triadic formula provides also interpretation of the effect of (cyano) substitutions. Let us examine why **1c** is more acidic than **1a**. Although their anions obtained by deprotonation are the same, we shall retain their labels **c** and **a** in order to signify the site of the proton attack. The corresponding triad reads: APA(**1c**$^-$) – APA(**1a**$^-$) = [−21.6; 21.6; −14.6] = −14.6, implying that **1c** is more acidic because of the weaker C–H homolytic bond energy (BAE term). The effect of relaxation exactly cancels out the contribution of Koopmans' term as it should be, because they add up to the first adiabatic ionization energy of the anion **1**$^-$. It is interesting to observe that Koopmans' term, taken for itself, always lowers the acidity of the ***n*a** (n = 1–3) tautomers compared to the less stable ones. The reason is that the PRIMO is a HOMO frontier orbital in ***n*a**. In contrast, it is HOMO−1 for less stable tautomers (Fig. S8, ESI†), which has lower orbital energies. The same holds for the cyanated tautomer pairs for the same n like *e.g.* $\mathbf{1a_{CN}}$ and $\mathbf{1e_{CN}}$ (Fig. S8, ESI†). Let us select **1c** as a gauge system and consider changes ΔAPA(S$^-$) = APA(S$^-$) – APA(**1c**$^-$) induced by fusion of benzene rings for S$^-$ = **2e**$^-$ and **3g**$^-$. It turns out that annelation increases acidity ΔAPA(**2e**$^-$) = [−7.7; 3.0; −8.5] = −13.2 and ΔAPA(**3g**$^-$) = [−16.5; 9.8; −20.8] = −27.5 (in kcal mol^{-1}), which is a joint result of the initial and final state features. Notice that the effect is approximately additive in **3g**$^-$. The influence of the final state is obvious, since the PRIMO (*i.e.* HOMO−1) orbitals undergoing ionization are more stable in larger systems involving additional benzene ring(s). However, a decrease in the bond association energies BAEs deserves a comment. The reason behind is that deprotonation of the central nonplanar carbon triggers a significant reorganization due to planarization of the anion, accompanied by stabilization, which enters the C–H bond energy term by diminishing it, or *vice versa*, it causes deformation of the conjugate base by formation of the central tetracoordinate carbon. This is evident in all systems possessing acidic proton at the central C(sp^3) site be it polysubstituted by the CN groups or not. In particular, it explains a lower bond association energy in protonation of **1c**$^-$ relative to that of the cyclopentadiene anion **4**$^-$ discussed before (*vide supra*).

The effect of cyanation should be reflected the most in Koopmans' term. This is indeed the case as evidenced by ΔAPA($\mathbf{1e_{CN}}^-$) = [−91.3; 11.2; −4.0] = −84.1, ΔAPA($\mathbf{2l_{CN}}^-$) = [−95.3; 10.4; −9.2] = −94.1 and ΔAPA($\mathbf{3m_{CN}}^-$) = [−106.7; 18.2; −20.8] = −109.3 (in kcal mol^{-1}), where the stabilization of the PRIMOs is decisive diminishing APAs and increasing acidity by 84.1, 94.1 and 109.3 kcal mol^{-1}, respectively. The BAE term becomes more influential in amplifying acidity, if there is an additional benzene fragment, because the reorganization effect of the molecular fragment upon bond formation on the central carbon is larger for obvious reason. This term is doubled by each benzene fusion. Finally, let us consider decrease in acidity of the keteneimine prototropic tautomers. Since the latter always have the same final conjugate base as other tautomers, it suffices to examine the bond association term BAE. It is lower in the tautomer possessing central (distorted) tetrahedral C(sp^3)–H fragment, since the reorganization stabilization in this particular bond formation is higher. This is obvious in the model systems **5** and **6** (Table 2), where the reorganization energy is larger in **6** by 7.4 kcal mol^{-1} leading to its lesser acidity. Similarly, comparison of the BAE term in $\mathbf{1a_{CN}}$ and $\mathbf{1e_{CN}}$ as well as in $\mathbf{2a_{CN}}$ and $\mathbf{2l_{CN}}$ pairs of acids reveals the differences of 14.9 and 22.1 kcal mol^{-1}, respectively, which interprets in simple way lesser acidity of the more stable keteneimine tautomers. The same holds for the hyperacids $\mathbf{3a_{CN}}$ and $\mathbf{3b_{CN}}$ (Table 2).

Acidity in DMSO

The nonprotic solvents of low polarity have several advantageous features: they (1) exert a small perturbation on the solvated compound, (2) enable investigations of species of both low and high acidity and (3) provide a good model for technological processes, which in turn usually take place in nonpolar solvents. A suitable inert solvent of this kind is dimethyl sulfoxide (DMSO). Measurements in this medium are free from ion association effects[94] and the relative acidities do not depend on the choice of the reference acid due to its large dielectric constant.[95] For these reasons we examined also some of the relevant acids considered here in DMSO by using procedure described in the Theoretical methodology section. The calculated $\Delta_rH_{\rm DMSO}$ and estimated pK_a values obtained *via* eqn (4) are presented in Table 1. It appears that some molecules exhibit very low pK_a values like *e.g.* pK_a($\mathbf{1a_{CN}}$) = −22.6, pK_a($\mathbf{2a_{CN}}$) = −16.8 and pK_a($\mathbf{3a_{CN}}$) = −21.6 (in pK_a units). It is of interest to compare these values with the pK_a value in DMSO of H_2SO_4 considered by Gillespie and Peel[77] as a reference superacid. Since the experimental p-$K_a(H_2SO_4)_{\rm DMSO}$ = 1.99,[96] it follows that *e.g.* molecules $\mathbf{1a_{CN}}$, $\mathbf{2a_{CN}}$ and $\mathbf{3a_{CN}}$ are around 25, 19 and 24 orders of magnitude stronger acids in DMSO than H_2SO_4, respectively, which is remarkable. They would represent important rungs on the superacidity scale. It should be pointed out that the predicted pK_a value for fluoradene (**3a**) is 10.1, which is in very good agreement with the available experimental value of 10.5 obtained by Bordwell.[96] This is a circumstantial support for the theoretical results, but still an important one. It should be noted in passing that synthesis of less stable prototropic tautomer would provide much more powerful superacids in DMSO (Table 1). For instance, the least stable polycyanated fluoradene tautomer $\mathbf{3q_{CN}}$ would have the gas-phase deprotonation enthalpy as low as 215.0 kcal mol^{-1}, being 22 orders of magnitude more acidic than hyperacidity threshold provided by DMAN molecule. It is interesting to notice that acidity in DMSO does not linearly follow acidity in the gas-phase (GP). For example, $\mathbf{1e_{CN}}$ is more acidic in the GP than the series of related systems $\mathbf{1a_{CN}}$–$\mathbf{1d_{CN}}$. However, it is the least acidic among them in DMSO (pK_a($\mathbf{1a_{CN}}$) = −20.5), since it is more stabilized in this solvent than the rest of these compounds (Table 1).

Table 2 Proton affinities (PAs) of anions A^- and their dissection into components according to triadic formula (8) as obtained with B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) method. All values are in kcal mol^{-1}

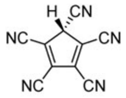
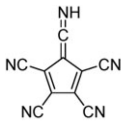
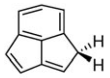
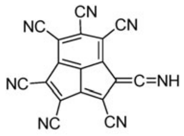
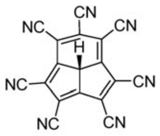
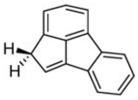
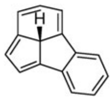
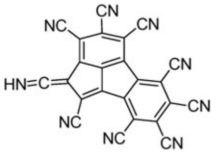
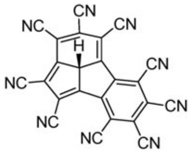
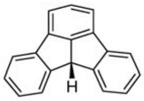
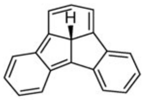
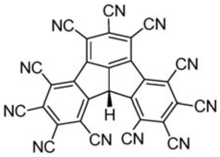
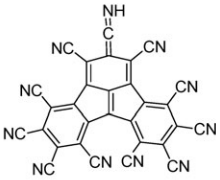
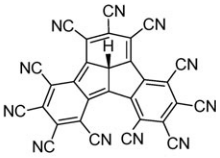
Molecule AH	$IE(A^-)_n^{Koop}$	$IE(A^-)_1^{ad}$	$E(ei)_{rex}$	BAE	$APA(A^-)$
 **4**	$(44.6)_1$	40.7	3.9	81.0	353.9
 **5**	$(144.4)_1$	127.4	17.0	70.1	256.3
 **6**	$(144.4)_1$	127.4	17.0	77.5	263.7
 **1a**	$(49.2)_1$	45.5	3.7	77.5	345.6
 **1c**	$(70.8)_2$	45.5	25.3	62.9	331.0
 **1a**$_{\mathbf{CN}}$	$(141.9)_1$	125.6	16.3	73.8	261.8
 **1e**$_{\mathbf{CN}}$	$(162.1)_2$	125.6	36.5	58.9	246.9
 **2a**	$(50.7)_1$	50.2	0.5	77.9	341.3
 **2e**	$(78.5)_2$	50.2	28.3	54.4	317.8

Table 2 (*continued*)

Molecule AH	$\mathrm{IE(A^-)}_n^{\mathrm{Koop}}$	$\mathrm{IE(A^-)}_1^{\mathrm{ad}}$	$E(\mathrm{ei})_{\mathrm{rex}}$	BAE	$\mathrm{APA(A^-)}$
 **2a$_{\mathbf{CN}}$**	$(144.0)_1$	130.4	13.6	75.8	259.0
 **2l$_{\mathbf{CN}}$**	$(166.1)_2$	130.4	35.7	53.7	236.9
 **3a**	$(50.7)_1$	52.2	–1.5	68.9	330.3
 **3g**	$(87.3)_2$	52.2	35.1	42.1	303.5
 **3a$_{\mathbf{CN}}$**	$(144.8)_1$	134.0	10.8	66.7	246.3
 **3b$_{\mathbf{CN}}$**	$(177.5)_2$	134.0	43.5	64.1	243.7
 **3m$_{\mathbf{CN}}$**	$(177.5)_2$	134.0	43.5	42.1	221.7

Concluding remarks

The main results can be summarized by focusing on the following important issues:

(1) Pure hydrocarbons **1a**, **2a** and **3a** are neutral C(sp^3)H acids of medium strength in the gas-phase as evidenced by the ΔH_{acid} values of 345.6, 341.3 and 330.3 kcal mol^{-1}, respectively. However, if their less stable prototropic tautomers are considered, then the acidity sharply increases. For instance, **3g** is even slightly more acidic in the gas-phase (ΔH_{acid}(**3g**) = 303.5 kcal mol^{-1}) than sulfuric acid ($\Delta H_{\mathrm{acid}}(H_2SO_4)$ = 306.3 kcal mol^{-1}). Interestingly, it is significantly more acidic in DMSO as reflected in their pK_a values of −7.3 and 1.99, correspondingly.

(2) Multiple cyanation dramatically increases acidity. Percyanated derivatives **1a$_{CN}$**, **2a$_{CN}$** and **3a$_{CN}$** possess the gas-phase ΔH_{acid} values as low as 261.8, 259.0 and 246.3 kcal mol^{-1}, respectively. It is important to realize that **1a$_{CN}$** and **2a$_{CN}$** are NH acids, since the acidic moiety is the keteneimine fragment. In contrast **3a$_{CN}$** is the CH acid with the C(sp^3) acidic site. If we accept the threshold of superacidity $\Delta H_{\mathrm{acid}}(HClO_4)$ = 300.0 kcal mol^{-1} and the protonation enthalpy of the first proton sponge 1,8-bis(dimethylamino)-naphthalene DMAN (PA(DMAN) = 245.3 kcal mol^{-1})[78] as a borderline for hyperstrong acidity, then it would be fair to say that **1a$_{CN}$** and **2a$_{CN}$** are strong superacids, whereas **3a$_{CN}$** qualifies as the first CH hyperacid designed *in silico*. It is found that percyanation amplifies acidity by 81–87 kcal mol^{-1}, depending on the system. The origin of dramatically increased acidity in polycyanated derivatives is identified as predominance of the anionic resonance effect in the conjugate bases, which are thus very stable. It involves a shift of the excess anionic electron density to the peripheral nitrogens and a slight increase in the density of the carbon atoms previously impoverished by the highly electronegative CN groups in the initial neutral acids. Since the excess anionic charge is strongly dispersed over all atoms of the conjugate base, it is plausible to assume that their nucleophilicity will be small. Stable anions with efficiently distributed negative charge might be very useful in a number of applications, as discussed at length by Strauss,[97] Gaiser and Schlueter[98] and Krossing and Raabe.[99] It is shown that **1a$_{CN}$**, **2a$_{CN}$** and **3a$_{CN}$** are strong superacids in DMSO.

(3) The structure of tricyclic 7b*H*-cyclopenta[*cd*]indene **1c** bridged by the central C(sp^3)H subunit reveals an almost uniform distribution of the C–C bond distances over the molecular perimeter strongly indicating its quasi-[10]annulene character, in spite of some nonplanarity caused by the tetracoordinate carbon atom. The role of this C(sp^3) carbon is of paramount importance, since it "freezes" the [10]annulene structure introducing the rigidity into the floppy "normal" [10]annulene.[75] The methyl substitution at this site prevents formation of the more stable tautomers. In contrast, considerable alternations of the CC bond lengths over the molecular rim are found in **2e** and **3g** systems, clearly showing that they do not represent elusive quasi-[14]- and [18]annulenes. These two molecules are obtained by annelation of one and two benzene moieties to the parent system **1c**, respectively, thus forming the molecular wing(s). This has important consequences, since the π-electron networks of **2e** and **3g** include significant contributions from the smaller circular π-electron substructures, which conform to the aromatic Hückel count rule. This finding is very important, because it reveals "philogenesis" of large molecules. They incorporate (modified) properties of smaller molecular subsystem(s), which can be considered as building blocks and predecessors. For instance, **3g** π-electron network involves inter alia 14π-electron and 10π-electron delocalization patterns obtained by the perfect pairing of the π-electrons over the molecular rims of smaller **2e** and **1c** free systems, respectively. It is extraordinary that Hückel's (4*n* + 2)π count rule is so useful in polycyclic π-systems at least for the book keeping purposes. This resembles Clar's π-electron sextet rule holding in condensed polycyclic aromatic (benzenes) hydrocarbons,[100,101] and represents its generalization.

It follows as a corollary that a synthesis of these polycyanated compounds is highly desirable and strongly recommended. Moreover, derivatives containing lesser number of cyano groups, complemented perhaps by other electron withdrawing substituents, could provide a plentitude of strong neutral (super)acids.

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