Strong Acidity of Some Polycyclic Aromatic Compounds Annulated to a Cyclopentadiene Moiety and Their Cyano Derivatives – A Density Functional B3LYP Study

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The acidity of the parent 1*H*-benz[*f*]indene (**1a**), 1*H*-benz[*e*]indene (**2a**), 1*H*-benz[*fg*]acenaphthylene (**3a**) and 1*H*-cyclopenta[*l*]phenanthrene (**4a**) and of their polycyano derivatives is examined in the gas phase and in DMSO by the DFT-B3LYP methods. It is shown that the parent hydrocarbons exhibit modest acidities, whereas a dramatic increase in acidity is observed upon multiple cyanation leading to hyperstrong neutral organic superacids. It is found that polycyano derivatives undergo prototropic tautomerism with a consequence that the most stable tautomer contains a ketene imine C=C=NH functionality. The origin of their highly pronounced acidity is identified as a very strong anionic resonance effect efficiently assisted by a large number of CN groups in a concerted manner. It is stressed that the polycyanated anions are very stable and have a highly dispersed negative charge, which should lead to a low nucleophilicity and weak coordinating properties, thus making them potentially very useful in academic research and technological applications.

Introduction

The proton transfer reactions belong to the most important chemical transformations in chemistry and biochemistry. In order to understand the proton transfer as a physical and chemical phenomenon, a wide knowledge of acidity and basicity of molecules is necessary together with a sound interpretation of both experimental and theoretical results. This is the reason why gathering of the thermodynamic data on Brønsted acidity and basicity has been at a focus of interest of numerous experimental researchers[1–3] and computational chemists[4,5] in the last several decades. As to the rationalization of proton affinities and deprotonation energies, it should be mentioned that a new trichotomy formula was introduced recently,[6–8] which offered a new insight into the nature of these fundamental chemical properties. Much attention has been laid on the design of potent neutral organic superacids lately.[9–18] Two new strategies in tailoring superacids have been developed. The first was based on the use of the electronic superacceptor substituents,[9,10] whereas the second utilized the concept of stabilization of the conjugate bases through very strong anionic resonance triggered by cyano substituents.[13–15] Both strategies have led to a large number of extremely powerful superacids both in the gas phase[9–15] and in solutions.[16,17] An interesting class of very strong acids is given by carboranes.[11,12] It should be stressed that strong organic acids and carboranes possess some distinct advantages over their mineral counterparts, since they are reactive in mild chemical environments. In particular, the superacids are pivotal in general acid catalysis.[19] Moreover, stable anions of superacids exhibiting chemical inertness and solubility proved very useful in applications including olefin polymerization[20] and the isolation of highly reactive short-lived cations like HC_{60}^+ and $C_{60}^{\cdot+}$,[21] $C_6H_7^+$,[22] Bu_3Sn^+[23] and $Cu(CO)_4^+$.[24] Consequently, synthesis of new superacids is highly desirable, because of their scientific and technological importance.

Obviously, it is important to form a dense ladder of new superacids in order to meet the needs mentioned above. In particular, it would be useful to have at disposal strong superacids, which would enter the domain of strong superbases[25–27] thus providing a unified scale of acids and bases. The interaction between superacids and superbases would eventually lead to a spontaneous proton transfer[28,29] and formation of new ion pairs.[30,31] Pursuing our efforts in this direction we report on the acidity of 1*H*-cyclopenta[*b*]naphthalene (**1a**), 1*H*-cyclopenta[*a*]naphthalene (**2a**), 3*H*-cyclopenta[*cd*]phenalene (**3a**) and 1*H*-cyclopenta[*l*]phenanthrene (**4a**) (Scheme 1) as predicted by the density functional theory (DFT). A salient feature of these compounds is the presence of a single C(sp^3) centre, which provides the most acidic position. Subsequently, the effect of polycyano substitutions will be examined. It will turn out

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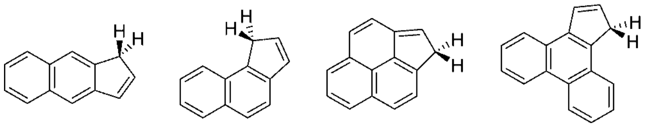
that the latter exerts a dramatic change in acidity leading to some extremal values in the gas phase and in DMSO. It is gratifying and very important to stress that the chemistry of the cyano group is well known,[32–34] and that the parent cyclopentadiene-annulated polycyclic aromatic hydrocarbons **1a**,[35–38] **2a**,[39,40] **3a**[41] and **4a**[42,43] have already been prepared and are known in the literature.



1a **2a** **3a** **4a**

Scheme 1.

Theoretical Methods

The gas-phase acidity is given by the enthalpy change, ΔH_{acid}, for the proton dissociation reaction [Equation (1)]:

$$AH(g) \rightarrow A^{-}(g) + H^{+}(g) \quad (1)$$

which is obtained as Equation (2):

$$\Delta H_{acid} = \Delta E_{acid} + \Delta(pV) \quad (2)$$

where ΔE_{acid} is the change in the total molecular energies of the species involved in reaction (1). It includes the total electronic energy and repulsion of the nuclei, the zero-point vibrational energy (ZPVE) and the finite (room) temperature correction at 298.15 K. The pressure-volume work is termed by $\Delta(pV)$ as customary. It is useful to keep in mind that stronger acids have smaller numerical values of ΔH_{acid}, which means easier release of the proton.

It is well documented that G2 and G3 computational schemes and their simplified versions G2(MP2) and G3(MP2) reproduce the experimental acidities with a very good accuracy.[4,5] Unfortunately, they are computationally too demanding to be used in the large systems **1a**–**4a** and their cyano derivatives. Hence, one has to resort to more practical methods, which represent a reasonable compromise between feasibility and reliability. One of the best choices is the DFT-B3LYP method,[44,45] provided a satisfactory basis set is employed. Handy and co-workers[46] have shown that Pople's triple-zeta basis sets including the polarization and diffuse functions yield practically converged energies at this level of the DFT approach. Hence, our method of choice was B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d), which implies that geometries are optimized by a very economical 6-31G(d) basis set, whereas energies are estimated by a flexible 6-311+G(2d,p) set necessary for description of anions. It should be pointed out that both B-LYP and B3-LYP functionals reproduce acidities rather well provided extended basis sets are used.[47,48] Moreover, Schaefer and co-workers have shown in a series of papers that the DFT methods are very useful in reproducing electron affinities of molecules, which is an important parameter in describing deprotonation.[49–53] This lends credence to the method employed here and puts all superacids examined so far on the same (theoretical) ladder.[13–15]

It is widely accepted that rigorous ab initio and modern DFT methods predict acidity and basicity of molecules quite accurately in the gas phase.[4,5,54] It is much more difficult to describe these two features in solutions. However, we found useful in this respect a simple polarized continuum model (PCM) developed by Miertuš and Tomasi,[55,56] which works well for both acidity[18] and basicity[57] in aprotic solvents of medium polarity. The cavity within a solvent embedding the solvated molecule is defined by the molecular surface with constant density of 0.0004 eB^{-3} as proposed by Wiberg and co-workers[58,59] thus giving rise for the isodensity polarized continuum model (IPCM). We shall apply this model in assessing the influence of the DMSO solvent molecules in solution on the acidity of compounds **1a**–**4a** and on their multiply substituted CN derivatives. Our calculations are based on the proton transfer reaction between solvated acids and the dimethyl sulfoxide molecules:

$$AH + DMSO \rightarrow A^{-} + DMSOH^{+} + \Delta_r H_{DMSO} \quad (3)$$

which results in the conjugate base A^{-}. The changes in the total molecular enthalpies of Equation (3) are denoted by $\Delta_r H_{DMSO}$. They are calculated by the IPCM/B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) model as mentioned above, by using the thermal correction obtained at the B3LYP/6-31G(d) level. It is noteworthy that extensive calculations and comparison with the measured acidities for a wide variety of neutral organic CH acids gave a very good correlation:

$$pK_a(\exp) = 0.661 \cdot \Delta_r H_{DMSO}(\mathrm{th}) - 7.7 \quad (4)$$

between the experimental pK_a values and computed $\Delta_r H_{DMSO}$ enthalpies.[18] A good agreement is evidenced by a relatively small average absolute error of 1.1 pK_a units and a relatively high correlation coefficient of $R^2 = 0.985$. This accuracy is sufficient for our purpose. Hence, Equation (4) will be employed in predicting pK_a values in DMSO of examined superacids.

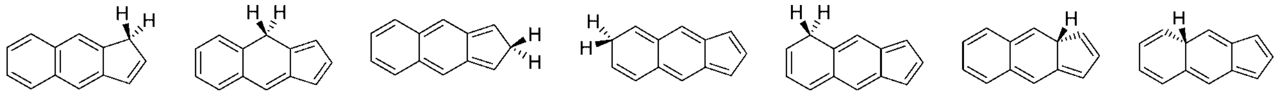
All calculations were performed with the GAUSSIAN98 program package.[60]

Results and Discussion

1*H*-Cyclopenta[*b*]naphthalene Systems

We shall dwell on the paradigmatic 1*H*-cyclopenta[*b*]-naphthalenes in some more detail in order to develop several rules of thumb, which will enable a condensed, but clear discussion of related systems later on. The parent 1*H*-cyclopenta[*b*]naphthalene has 7 tautomers (**1a**–**1g**), which are depicted in Figure 1. Their relative energies are calculated by the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) model as well as with the more economical B3LYP/6-31G(d) level of theory.

It appears that **1a** is substantially more stable than other tautomers, because the π-electron distribution pattern over

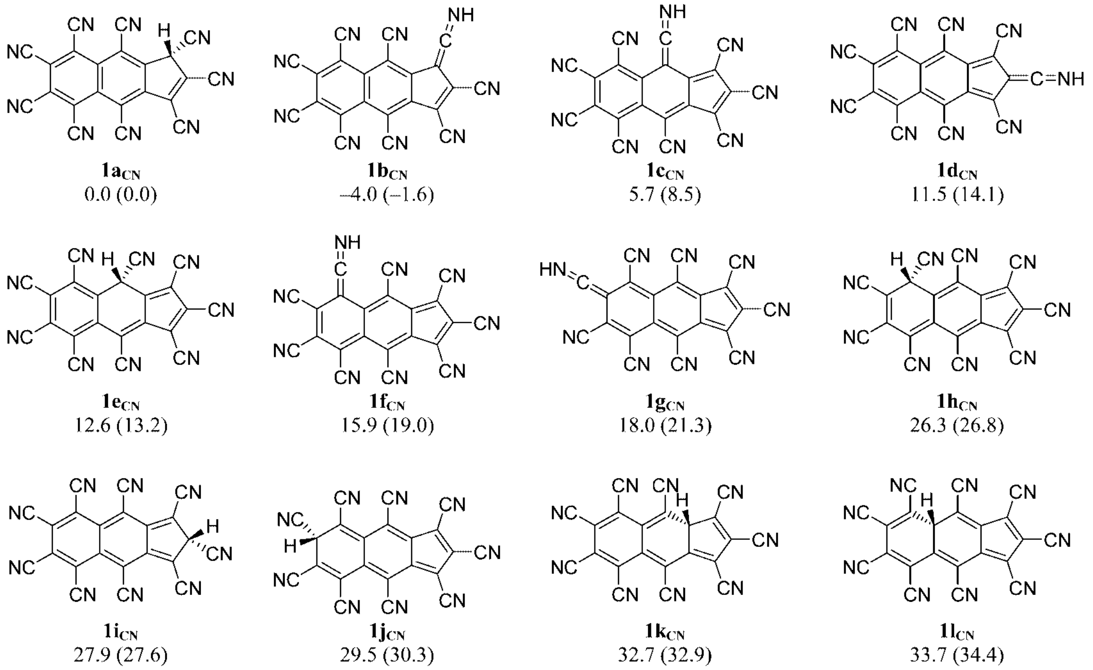


1a 0.0 (0.0)
1b 19.5 (19.9)
1c 31.5 (32.3)
1d 34.9 (35.9)
1e 37.6 (38.3)
1f 44.9 (46.6)
1g 48.8 (50.8)

Figure 1. Schematic representation of 1*H*-cyclopenta[*b*]naphthalene 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 in parentheses (in kcal mol^{-1}).

the naphthalene fragment is the same as in naphthalene itself. The second most stable tautomer (**1b**) has a higher energy by 19.5 kcal mol^{-1}, since the π-electron motif of naphthalene is lost, but the aromatic sextet of the left six-membered ring is preserved. All other tautomers are less stable because they do not contain the aromatic fragment, being sometimes additionaly strained by introduction of nonplanarity through the C(sp^3) tertiary carbon atom (**1f** and **1g**). It goes without saying that nonplanarity hampers efficient π-AOs' overlapping, thus diminishing the conjugative effect. It is useful to notice that all tautomers **1a**–**1g** end up in the same anion upon deprotonation at the C(sp^3) atom. Therefore, we shall give only ΔH_{acid} of the most stable tautomer **1a**, being 348.6 kcal mol^{-1}. The ΔH_{acid} values of other tautomers are lower by the difference in their ground state energies. This means that ΔH_{acid}(**1a**) = 348.6 kcal mol^{-1} is the upper bound for the whole series, or alternatively, it implies that acidity increases along tautomers **1a**–**1g**. Since the resulting anion (conjugate base) representing the final state is identical in all cases, it follows that the variation in acidity along the series is determined by the properties of the initial states (i.e. by the neutral acids). This is a general characteristic of all families of closely related compounds studied in the present work. It does not hold, however, for the widely different families of molecules as, for example, between the parent hydrocarbons and their heavily substituted derivatives (vide infra), or systems possessing different backbones.

It appears that the initial compound **1a** is moderately acidic. In contrast, **1g** would give a very strong acid, if prepared in the laboratory. It is of some interest to compare the acidity of **1a** with that of cyclopentane, cyclopentene and cyclopentadiene. Their corresponding ΔH_{acid} values are 412.7, 393.8 and 352.6 kcal mol^{-1}, respectively. It should be pointed out that all values refer to the C(sp^3)H center and that in the case of cyclopentene deprotonation takes place at the methylene group vicinal to the double bond, thus enabling the anionic resonance within the allylic moiety in the conjugate base. In order to estimate the latter, we need the deprotonation energy at the distal CH$_2$ site, which yields ΔH_{acid} of 414.1 kcal mol^{-1}, being close to that in cyclopentane. The problem is, however, the nonplanarity of the cyclopentene anion obtained by the heterolytic cleavage at position C-4, since the lone pair prefers an appreciable amount of the s-character. Hence, we shall consider a model system with planar C-4 carbon atom after deprotonation, which gives ΔH_{acid} of 417.9 kcal mol^{-1}. It follows that the anionic resonance contributes 24.1 kcal mol^{-1} to the acidity of cyclopentene deprotonated at the C-3 position. Interestingly, the ΔH_{acid} of cyclopentadiene is by 65.3



1a$_{CN}$ 0.0 (0.0)
1b$_{CN}$ –4.0 (–1.6)
1c$_{CN}$ 5.7 (8.5)
1d$_{CN}$ 11.5 (14.1)
1e$_{CN}$ 12.6 (13.2)
1f$_{CN}$ 15.9 (19.0)
1g$_{CN}$ 18.0 (21.3)
1h$_{CN}$ 26.3 (26.8)
1i$_{CN}$ 27.9 (27.6)
1j$_{CN}$ 29.5 (30.3)
1k$_{CN}$ 32.7 (32.9)
1l$_{CN}$ 33.7 (34.4)

Figure 2. Prototropic tautomers of polycyano derivatives of 1*H*-cyclopenta[*b*]naphthalene. 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.

kcal mol^{-1} lower than that of the cyclopentane model system with a planar C-4 anionic center. A simple additivity of the two isolated double bonds in the five-membered ring framework, such as in two cyclopentenes, would yield only 48.2 kcal mol^{-1} implying that additional 17.2 kcal mol^{-1} is obtained by the cyclic aromatic stabilization of the cyclopentadienyl anion. Finally, it appears that $\Delta H_{\mathrm{acid}}(\mathbf{1a})$ is lower by 4 kcal mol^{-1} than that of cyclopentadiene. Since the C(sp^3)H bond energies should be similar in both molecules, the difference can be attributed to a larger stability of the $\mathbf{1a}^-$ anion. This follows also from the count of the anionic resonance structures (not shown here).

The nonacyano derivatives ($\mathbf{1a_{CN}}$–$\mathbf{1l_{CN}}$) (Figure 2) exhibit an interesting prototropic tautomerism observed also in other polycyanated planar hydrocarbons possessing HC(sp^3)–CN nonplanar groupings.[13–15] It should be noticed that the polycyano derivative of the most stable parent hydrocarbon tautomer $\mathbf{1a_{CN}}$ will be taken as a reference in this family of compounds and similarly in other families later on.

This is important to bear in mind, because the reference compound is not the most stable one. Namely, the hydrogen atom can be attached to the nitrogen atom, thus forming a ketene imine functionality by a hydrogen walk from the C(sp^3) center to the nitrogen atom of the CN group bonded to the same C(sp^3) carbon atom. This type of the hydrogen shift yields the most stable tautomer in all cases,[13–15] which makes an interesting rule governing the hierarchy in stability of the prototropic tautomers. Hence, it is not surprising that tautomer $\mathbf{1b_{CN}}$ is also more stable than $\mathbf{1a_{CN}}$, albeit by only 4.0 kcal mol^{-1}. It is noteworthy that both tautomers retain the π-electron partial localization pattern of naphthalene in the corresponding fragment. The least stable tautomers are $\mathbf{1k_{CN}}$ and $\mathbf{1l_{CN}}$, since they contain a distorted tertiary C(sp^3) atom, which induces nonplanarity that reduces the π-electron conjugation. The rest of the tautomers occur in pairs in decreasing order of stability of the first tautomer in parentheses: ($\mathbf{1c_{CN}}$, $\mathbf{1e_{CN}}$), ($\mathbf{1d_{CN}}$, $\mathbf{1i_{CN}}$), ($\mathbf{1f_{CN}}$, $\mathbf{1h_{CN}}$) and ($\mathbf{1g_{CN}}$, $\mathbf{1j_{CN}}$). It should be noticed that a tautomer including the ketene imine C=C=NH moiety is always more stable than that involving the HC(sp^3)–CN grouping within the same pair. The difference in their stability varies between 5.8 and 15.3 kcal mol^{-1}. One of the reasons behind this increase in stability is the fact that the C=C bond of the ketene imine C=C=NH functionality becomes a part of the extended π-electron network, thus amplifying the π-electron conjugation.

The increase in acidity upon cyanation is spectacular. The ΔH_{acid} values for $\mathbf{1a_{CN}}$ and $\mathbf{1b_{CN}}$ are 256.9 and 261.8 kcal mol^{-1}, respectively (Table 1). They are powerful superacids indeed as evidenced by comparison with the well-known mineral strong Brønsted acids like HNO_3, H_2SO_4 and $HClO_4$. Their experimental gas-phase ΔH_{acid} values are 324.5, 306.3 and 288.0 kcal mol^{-1}, respectively.[1] Consequently, the acidity of $\mathbf{1b_{CN}}$ is around 33 orders of magnitude larger than that of H_2SO_4. A comparison with H_2SO_4 is particularly in place, since this molecule was used by Gillespie and Peel[61] as a threshold for superacids. The latter are defined as substances more acidic than 100% sulfuric acid. Although the definition of Gillespie and Peel pertains to solutions, a comparison of the gas-phase values is indicative. A similar comparison will be made in DMSO in the last but one paragraph. It should be noted in passing that $\Delta H_{\mathrm{acid}}(\mathbf{1b_{CN}})$ is the upper bound for the polycyanated series $\mathbf{1a_{CN}}$–$\mathbf{1l_{CN}}$. Acidities of other tautomers are higher and the corresponding values are easily deduced by using their relative stabilities given in Figure 2. For instance, $\Delta H_{\mathrm{acid}}(\mathbf{1l_{CN}})$ is very low, being 224.0 kcal mol^{-1}. The variation in acidity across the $\mathbf{1a_{CN}}$–$\mathbf{1l_{CN}}$ series is determined by the energetic properties of the initial acids. In contrast, the difference in acidity between the parent molecule **1a** and its nonacyano derivative $\mathbf{1a_{CN}}$ is a consequence of their final states. Namely, it is given by a difference in stability of $\mathbf{1a}^-$ and $\mathbf{1a_{CN}}^-$ anions. The former is stabilized by the anionic resonance effect of the aromatic 14π electrons as easily deduced by the resonance structures and distribution of the π-electron densities mirrored by the MO π-bond orders (not shown here). The matter of fact is that the anionic resonance in $\mathbf{1a_{CN}}^-$ is dramatically enhanced by the cyano groups, which immensely increase the number of resonance structures. This is a general phenomenon observed earlier,[13–15] which is corroborated by the present data. It occurs that the anionic resonance stabilizes both aromatic and antiaromatic anions being strongly supported by the cyano groups (vide infra).

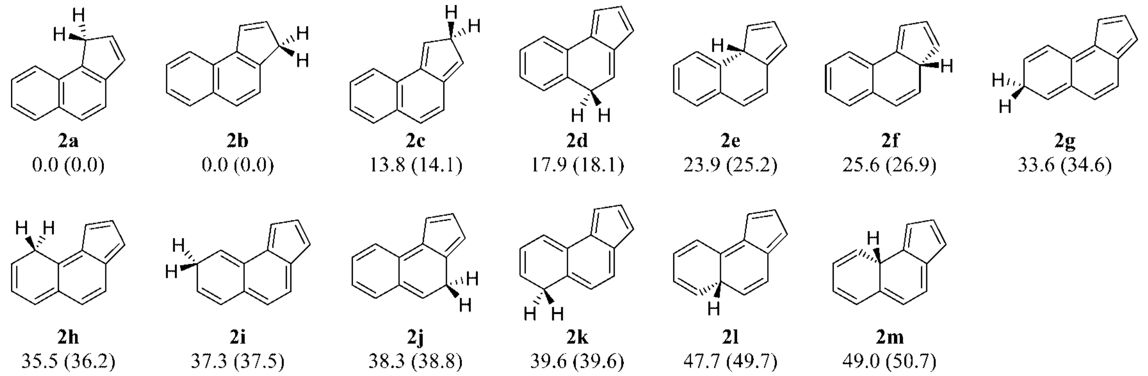
Table 1. Total molecular energies of studied molecules in the gas phase (GP) and in dimethyl sulfoxide (DMSO) obtained by the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) method. H_{corr} denotes thermal correction to enthalpy obtained by the B3LYP/6-31G(d) model. Theoretical pK_{a} values are obtained using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

Molecule	$-E_{\mathrm{GP}}$[a]	$-E_{\mathrm{DMSO}}$[a]	H_{corr}[a]	ΔH_{acid}[b]	$\Delta_{\mathrm{r}}H_{\mathrm{DMSO}}$[b]	pK_{a}(thr)[b]
1a	501.54313	501.55163	0.19782	348.6	42.0	20.1
$\mathbf{1a}^-$	500.97494	501.06148	0.18282			
$\mathbf{1a_{CN}}$	1331.84119	1331.88859	0.19884	256.9	–20.4	–21.2
$\mathbf{1a_{CN}}^-$	1331.42178	1331.50050	0.18649			
$\mathbf{1b_{CN}}$	1331.84838	1331.94474	0.19816	261.8	–15.3	–17.8
$\mathbf{1b_{CN}}^-$	1331.42178	1331.50050	0.18649			
2a	501.54162	501.54826	0.19771	343.8	38.9	18.0
$\mathbf{2a}^-$	500.98154	501.06345	0.18309			
$\mathbf{2a_{CN}}$	1331.84618	1331.92538	0.19810	263.0	2.5	–6.0
$\mathbf{2a_{CN}}^-$	1331.41808	1331.50177	0.18669			
$\mathbf{2b_{CN}}$	1331.84794	1331.90068	0.19814	264.0	–13.0	–16.3
$\mathbf{2b_{CN}}^-$	1331.41808	1331.50177	0.18669			
3a	577.77418	577.78020	0.21104	332.3	29.0	11.5
$\mathbf{3a}^-$	577.23287	577.31170	0.19695			
$\mathbf{3a_{CN}}$	1408.08049	1408.13488	0.21215	244.2	–23.9	–23.5
$\mathbf{3a_{CN}}^-$	1407.68188	1407.75297	0.20042			
$\mathbf{3b_{CN}}$	1408.09265	1408.13987	0.21166	252.2	–20.4	–21.2
$\mathbf{3b_{CN}}^-$	1407.68188	1407.75297	0.20042			
4a	655.22429	655.23765	0.24748	339.7	32.1	13.5
$\mathbf{4a}^-$	654.67069	654.76357	0.23285			
$\mathbf{4a_{CN}}$	1670.01469	1670.06330	0.24804	249.1	–20.3	–21.1
$\mathbf{4a_{CN}}^-$	1669.60790	1669.67523	0.23586			
$\mathbf{4b_{CN}}$	1670.02197	1670.07094	0.24728	254.1	–15.0	–17.6
$\mathbf{4b_{CN}}^-$	1669.60790	1669.67523	0.23586			

[a] In atomic units. [b] In kcal mol^{-1}.

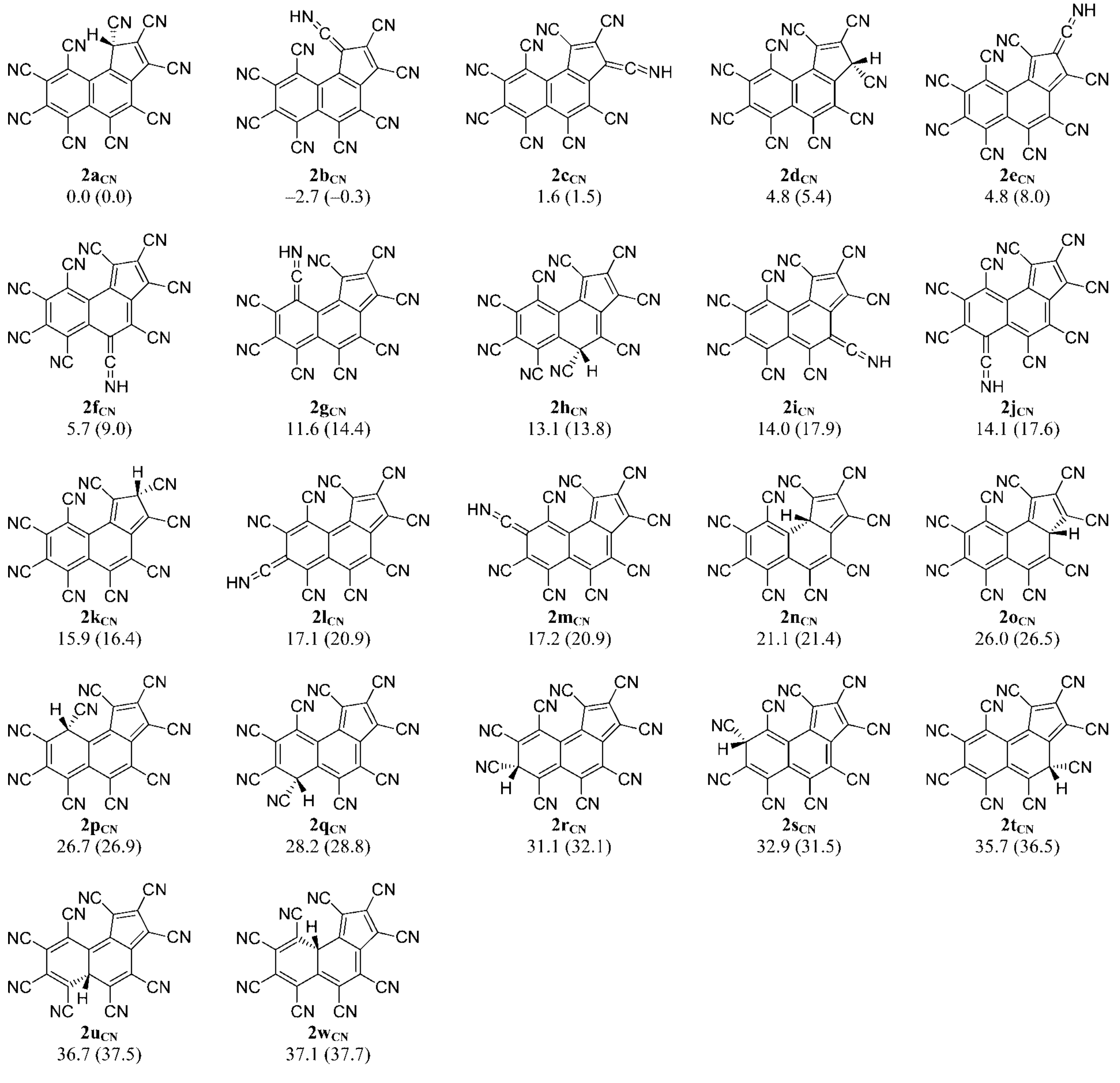
1*H*-Cyclopenta[*a*]naphthalene Systems

The parent 1*H*-cyclopenta[*a*]naphthalene exists in two tautomeric forms **2a** and **2b**, which fortuitously have the same total molecular energies (Figure 3).



2a 0.0 (0.0)
2b 0.0 (0.0)
2c 13.8 (14.1)
2d 17.9 (18.1)
2e 23.9 (25.2)
2f 25.6 (26.9)
2g 33.6 (34.6)
2h 35.5 (36.2)
2i 37.3 (37.5)
2j 38.3 (38.8)
2k 39.6 (39.6)
2l 47.7 (49.7)
2m 49.0 (50.7)

Figure 3. Schematic representation of 1*H*-cyclopenta[*a*]naphthalene 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$_{\text{CN}}$ 0.0 (0.0)
2b$_{\text{CN}}$ –2.7 (–0.3)
2c$_{\text{CN}}$ 1.6 (1.5)
2d$_{\text{CN}}$ 4.8 (5.4)
2e$_{\text{CN}}$ 4.8 (8.0)
2f$_{\text{CN}}$ 5.7 (9.0)
2g$_{\text{CN}}$ 11.6 (14.4)
2h$_{\text{CN}}$ 13.1 (13.8)
2i$_{\text{CN}}$ 14.0 (17.9)
2j$_{\text{CN}}$ 14.1 (17.6)
2k$_{\text{CN}}$ 15.9 (16.4)
2l$_{\text{CN}}$ 17.1 (20.9)
2m$_{\text{CN}}$ 17.2 (20.9)
2n$_{\text{CN}}$ 21.1 (21.4)
2o$_{\text{CN}}$ 26.0 (26.5)
2p$_{\text{CN}}$ 26.7 (26.9)
2q$_{\text{CN}}$ 28.2 (28.8)
2r$_{\text{CN}}$ 31.1 (32.1)
2s$_{\text{CN}}$ 32.9 (31.5)
2t$_{\text{CN}}$ 35.7 (36.5)
2u$_{\text{CN}}$ 36.7 (37.5)
2w$_{\text{CN}}$ 37.1 (37.7)

Figure 4. Prototropic tautomerism of polycyano 1*H*-cyclopenta[*a*]naphthalene. 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.

They are less stable than their 1*H*-cyclopenta[*b*]naphthalene (**1a**) counterpart by 0.9 kcal mol^{-1}. Both tautomers preserve the π-electron distribution of a free naphthalene in the corresponding aromatic fragment. They are followed in stability by tautomers **2c** and **2d**, which contain a benzene moiety and retain planarity of the carbon skeleton. It is interesting to draw attention to the fact that **2e** and **2f** come next despite a nonplanar tertiary carbon atom within the skeleton. However, they involve an aromatic benzene ring, which underlines the importance of aromaticity in determining the stability of the compounds. The last set of compounds **2g**–**2m** possesses essentially polyenic structure without an aromatic substructure and involves in some cases a nonplanar tertiary carbon atom center. The relative stabilities of 13 tautomers are given in Figure 3.

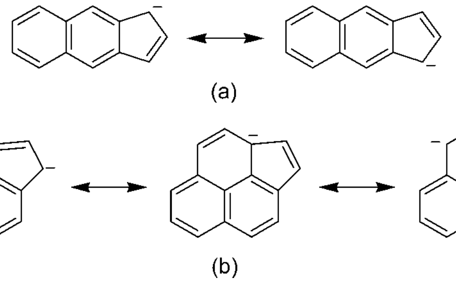
The ΔH_{acid} value for **2a** and **2b** is 343.8 kcal mol^{-1}, which is by 4.8 kcal mol^{-1} lower than that of **1a**. Since the final (aromatic 14 π-electrons) anion is the same in all three cases, it follows that the increase in acidity is a consequence of the initial state. The nine-fold cyanation leads to 22 prototropic tautomers depicted in Figure 4 together with their relative stabilities.

The structure containing a ketene imine functionality ($\mathbf{2b_{CN}}$) is the most stable one, although its total energy is only slightly lower than that of the reference polycyano derivative $\mathbf{2a_{CN}}$ (by –2.7 kcal mol^{-1}). Their ΔH_{acid} values are 263.0 ($\mathbf{2a_{CN}}$) and 264.0 ($\mathbf{2b_{CN}}$) in kcal mol^{-1}, which are somewhat higher than those of $\mathbf{1a_{CN}}$ and $\mathbf{1b_{CN}}$. Nevertheless, they represent useful rungs on the ladder of very strong superacids. The origin of the highly pronounced acidity is again the anionic resonance strongly supported by nine cyano groups.

3*H*-Cyclopenta[*cd*]phenalenes

The parent hydrocarbon 3*H*-cyclopenta[*cd*]phenalene tautomers are shown in Figure 5.

Their relative stabilities are easily understood by using the rule of thumb previously described. A striking difference with other systems examined here is given by the antiaromatic number of 16π electrons in their anionic deprotonated form. In spite of that, the ΔH_{acid}(**3a**) value is 332.3 kcal mol^{-1} implying that **3a** is considerably more acidic than **1a** and **2a**. This calls for an explanation. It is offered by a stronger anionic resonance effect in **3a**$^{-}$ compared to that in **1a**$^{-}$ (and **2a**$^{-}$) anion. This is reflected in a larger number of resonance structures, but it suffices to consider only those which retain the aromatic naphthalene π-electron pattern (Scheme 2).



Scheme 2. Leading resonance structures in anions **1a**$^{-}$ (a) and **3a**$^{-}$ (b).

It appears that the **3a**$^{-}$ anion has three such resonance structures, whereas the **1a**$^{-}$ anion has only two of them. Hence, it seems that the antiaromatic 4*n*π number of electrons does not necessarily imply destabilization in polycyclic anions. On the contrary, the 16π-electron system in **3a**$^{-}$ is more stable than the 14π-electrons network in **1a**$^{-}$. The nine-fold cyanation of **3a** leads to an enormous acidification of the reference polycyano derivative as reflected by $\Delta H_{acid}(\mathbf{3a_{CN}})$ = 244.2 kcal mol^{-1} (Figure 6).

It appears that the CN polysubstitution decreases the ΔH_{acid} value by 88 kcal mol^{-1}. This is comparable to the decrease in the ΔH_{acid} value of $\mathbf{1a_{CN}}$ relative to that of the parent **1a** system, being 91 kcal mol^{-1}. It follows that nine CN groups stabilize the aromatic 14π-electron system in polycyclic $\mathbf{1a_{CN}}^{-}$ by practically the same amount as the antiaromatic 16π electrons in polycyclic $\mathbf{3a_{CN}}^{-}$. It follows as a corollary that the global anionic resonance effect assisted by a larger number of substituent CN groups is very strong and equally important in 4*n*π and (4*n* + 2)π polycyclic systems. The ΔH_{acid} values for the rest of tautomers are easily deduced from the data given in Figure 6. It is important to stress that $\mathbf{3a_{CN}}$ and $\mathbf{3b_{CN}}$ belong to the most acidic compounds considered so far, if the reference and the most stable polycyano tautomers are taken into account only.

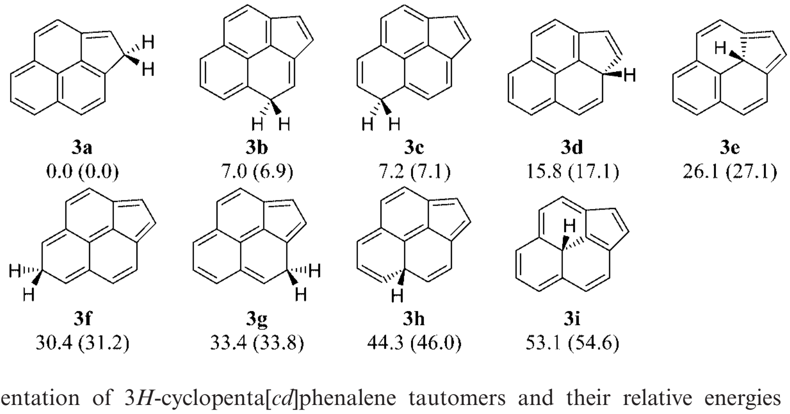
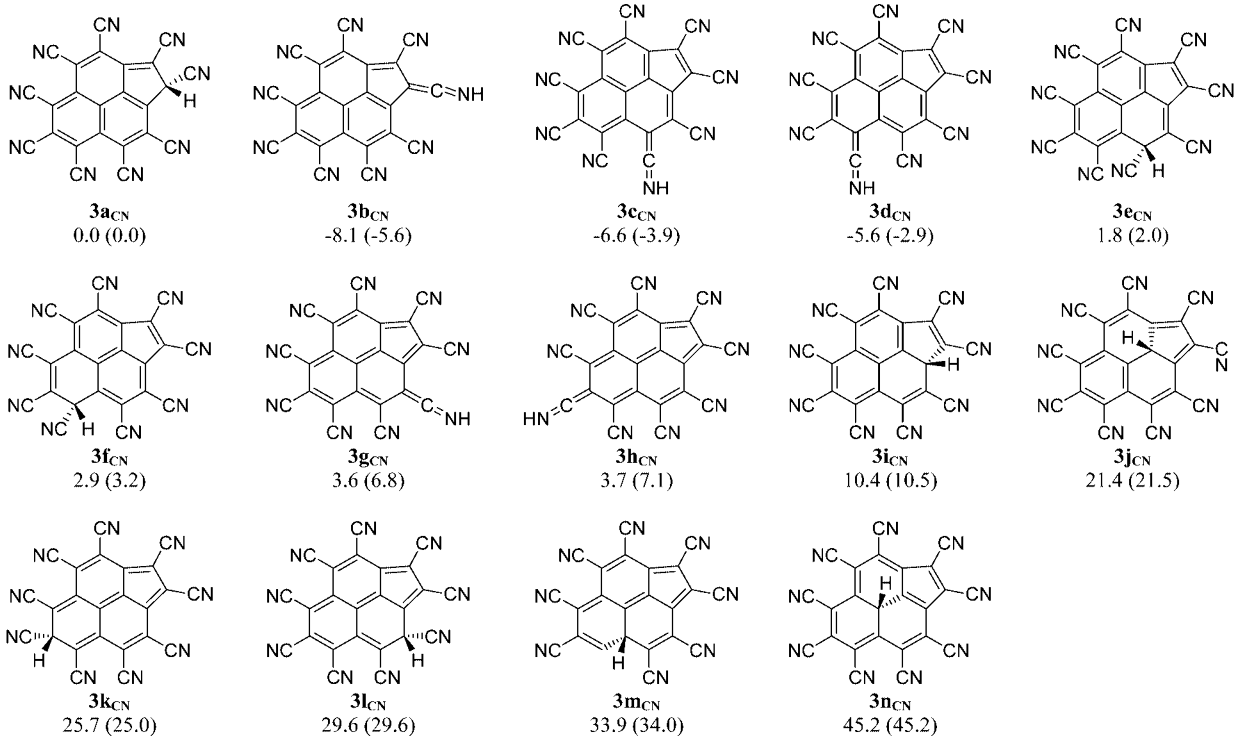


Figure 5. Schematic representation of 3*H*-cyclopenta[*cd*]phenalene tautomers and their relative energies obtained by the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) and B3LYP/6-31G(d) models. The latter are given within parentheses (in kcal mol^{-1}).



3a$_{CN}$ 0.0 (0.0)
3b$_{CN}$ -8.1 (-5.6)
3c$_{CN}$ -6.6 (-3.9)
3d$_{CN}$ -5.6 (-2.9)
3e$_{CN}$ 1.8 (2.0)
3f$_{CN}$ 2.9 (3.2)
3g$_{CN}$ 3.6 (6.8)
3h$_{CN}$ 3.7 (7.1)
3i$_{CN}$ 10.4 (10.5)
3j$_{CN}$ 21.4 (21.5)
3k$_{CN}$ 25.7 (25.0)
3l$_{CN}$ 29.6 (29.6)
3m$_{CN}$ 33.9 (34.0)
3n$_{CN}$ 45.2 (45.2)

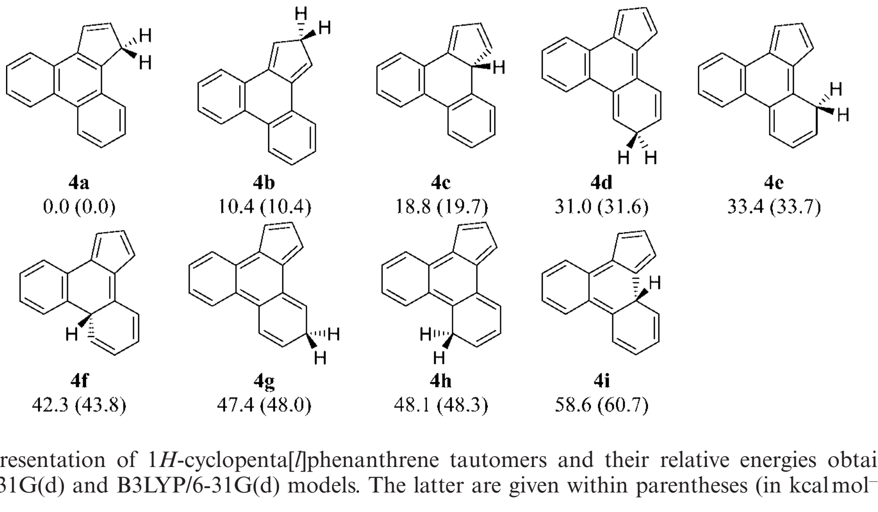
Figure 6. Prototropic tautomerism in polycyano-substituted 3*H*-cyclopenta[*cd*]phenalene. The relative stabilities (in kcal mol^{-1}) are calculated by the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) (B3LYP/6-31G(d)) methods.

1*H*-Cyclopenta[*l*]phenanthrenes

Nine 1*H*-cyclopenta[*l*]phenanthrene tautomers are presented in Figure 7.

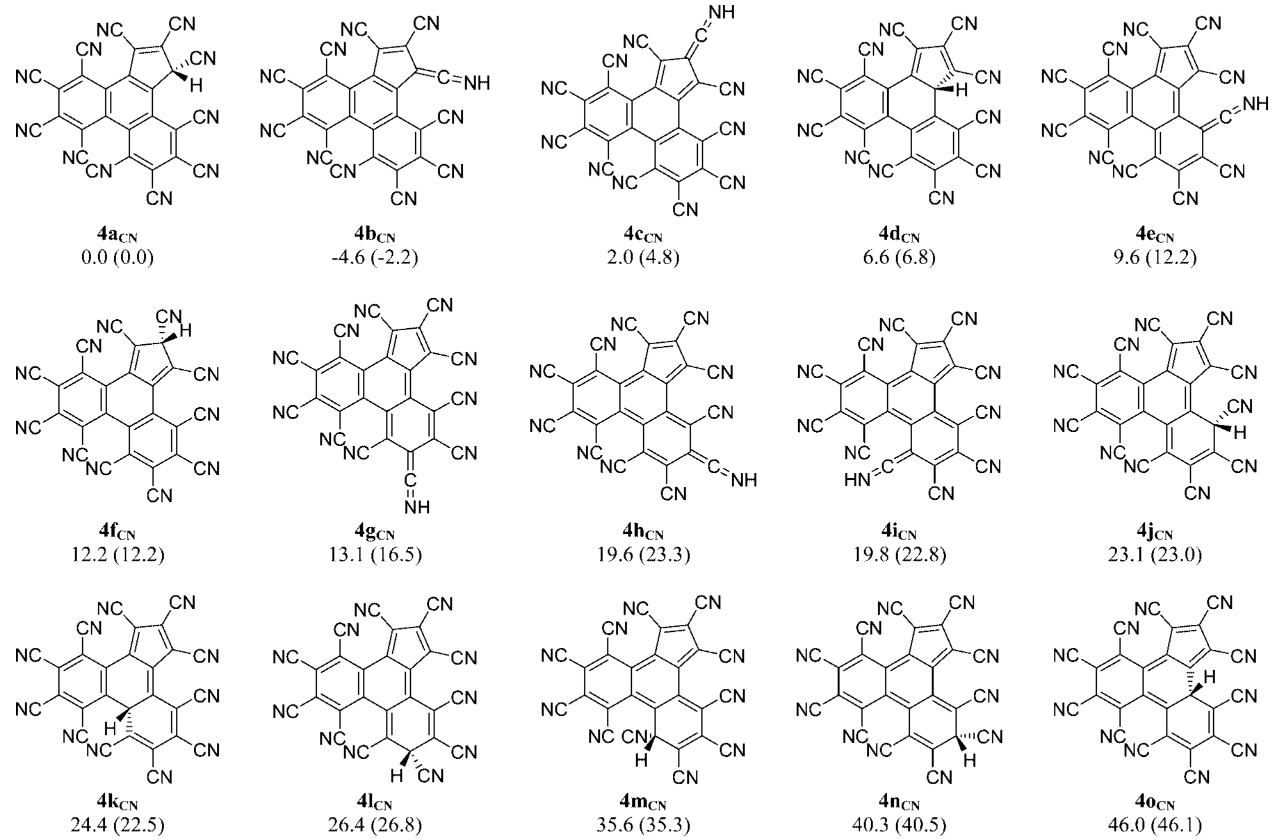
The most stable one is **4a**, since it retains a phenanthrene distribution of the π-bonds over the aromatic backbone. Its ΔH_{acid} value is 339.7 kcal mol^{-1}, which is by 7 kcal mol^{-1} higher than ΔH_{acid}(**3a**) = 332.3 kcal mol^{-1}. The lower acidity of **4a** is easily, albeit only qualitatively, rationalized by only two resonance structures in the **4a**$^{-}$ anion, which preserve the phenanthrene π-electron pattern compared to three resonance structures in the **3a**$^{-}$ anion containing a naphthalene-like substructure (Scheme 2). The eleven-fold CN substitution in **4a$_{CN}$** (Figure 8) leads to a dramatic increase in acidity as evidenced by ΔH_{acid}(**4a$_{CN}$**) = 249.1 kcal mol^{-1} (Table 1).

In other words, the cyano substitution decreases ΔH_{acid} by 90.6 kcal mol^{-1}, which is comparable to that observed in **1a$_{CN}$** and **3a$_{CN}$** earlier. We note in passing that **4a**$^{-}$ and **4a$_{CN}$**$^{-}$ anions have aromatic 18π electrons distributed over the polycyclic carbon framework. The lower acidity of the more stable **4b$_{CN}$** prototropic tautomer is a consequence of different energetic properties of the initial **4a$_{CN}$** and **4b$_{CN}$** acids. In other words, it is a result of the initial state effect. Still, the acidity of the latter is very high as evidenced by



4a 0.0 (0.0)
4b 10.4 (10.4)
4c 18.8 (19.7)
4d 31.0 (31.6)
4e 33.4 (33.7)
4f 42.3 (43.8)
4g 47.4 (48.0)
4h 48.1 (48.3)
4i 58.6 (60.7)

Figure 7. Schematic representation of 1*H*-cyclopenta[*l*]phenanthrene 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}).



$\mathbf{4a_{CN}}$ 0.0 (0.0)

$\mathbf{4b_{CN}}$ -4.6 (-2.2)

$\mathbf{4c_{CN}}$ 2.0 (4.8)

$\mathbf{4d_{CN}}$ 6.6 (6.8)

$\mathbf{4e_{CN}}$ 9.6 (12.2)

$\mathbf{4f_{CN}}$ 12.2 (12.2)

$\mathbf{4g_{CN}}$ 13.1 (16.5)

$\mathbf{4h_{CN}}$ 19.6 (23.3)

$\mathbf{4i_{CN}}$ 19.8 (22.8)

$\mathbf{4j_{CN}}$ 23.1 (23.0)

$\mathbf{4k_{CN}}$ 24.4 (22.5)

$\mathbf{4l_{CN}}$ 26.4 (26.8)

$\mathbf{4m_{CN}}$ 35.6 (35.3)

$\mathbf{4n_{CN}}$ 40.3 (40.5)

$\mathbf{4o_{CN}}$ 46.0 (46.1)

Figure 8. Prototropic tautomerism in polycyano derivatives of 1*H*-cyclopenta[*l*]phenanthrene. 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.

$\Delta H_{\text{acid}}(\mathbf{4a_{CN}})$ = 254.1 kcal mol^{-1} (Table 1); thus, it belongs to a class of ultrastrong superacids.

Acidities in DMSO

Behavior of superacids in nonprotic solvents of low and medium polarity is of utmost importance, since the main body of chemical reactions take place in solutions and because the nonpolar solvents have a number of favourable features. They involve inter alia a small perturbation of the studied solvated acids, which encompasses species of both very low and very high acidity. They provide good models for technological processes, which are usually realized in nonpolar solvents. Large planar polycyano-substituted hydrocarbons are particularly suitable for this purpose, since the anionic negative charge is distributed over many centers by the mobile π-electrons. The absence of the highly localized negative charge, which occurs in strong mineral acids as a rule, prevents excessive aggregation of solutes, which is a highly desirable feature. It was shown that DMSO is a very convenient solvent, because it enables measurements of acidities free of ion associations.[62] Concomitantly, DMSO is a strongly dissociating solvent with a large dielectric constant implying that the relative acidities do not depend on the reference acid. Taking the foregoing into acount, we examined the acidities of the most powerful superacids and their hydrocarbon parents in DMSO by using the proton transfer reaction (3) and the IPCM model described above. The resulting $\Delta_r H_{\text{DMSO}}$ enthalpies are presented in Table 1. They are negative for polycyano derivatives, meaning that the proton transfer to the solvent DMSO molecules is strongly favored. The pK_a values for the parent hydrocarbons **1a**, **2a**, **3a** and **4a** are 20.1, 18.0, 11.5 and 13.5, respectively, which indicates that the former two compounds are moderately acidic. The latter two species exhibit a significant increase in acidity. The fact that **3a** is more acidic than **4a** is compatible with its lower ΔH_{acid} value in the gas phase and its smaller molecular volume, which is also one of the factors determining the acidity in solutions. This is in harmony with an early observation of Taft and Bordwell,[63] who concluded that the solvation effects stabilize the smaller anions of the CH acids in DMSO more than the larger ones.

Let us focus now on the reference molecule and the most acidic polycyano derivatives ordered in the following pairs ($\mathbf{1a_{CN}}$, $\mathbf{1b_{CN}}$), ($\mathbf{2a_{CN}}$, $\mathbf{2b_{CN}}$), ($\mathbf{3a_{CN}}$, $\mathbf{3b_{CN}}$) and ($\mathbf{4a_{CN}}$, $\mathbf{4b_{CN}}$). Their pK_a values read: (–21.2, –17.8), (–6.0, –16.3), (–23.5, –21.2) and (–21.1, –17.6), respectively. Hence, it follows that polycyano derivatives are hyperstrong acids both in the gas phase and in DMSO. It is noteworthy that the most acidic system is provided by the 3*H*-cyclopenta[*cd*]phenalene backbone in its polycyanated $\mathbf{3a_{CN}}$ and $\mathbf{3b_{CN}}$ forms. Both tautomers are more acidic than the most potent neutral organic superacids considered by us so far: pentacyanocyclopentadiene, which has pK_a = –20.2 in DMSO. It is of interest to compare these values with the pK_a value in DMSO of H_2SO_4 considered by Gillespie and Peel[61] as a reference superacid. Since the experimental p$K_a(H_2SO_4)_{DMSO}$ = 1.99,[64] it follows that **3a$_{CN}$** and **3b$_{CN}$** are around 25 and 23 orders of magnitude stronger acids in DMSO than H_2SO_4, respectively, which is remarkable indeed. Similarly, it appears that **1b$_{CN}$** is by 20 orders of magnitude more acidic than H_2SO_4 in DMSO. The corresponding difference in the gas phase was larger (33 orders of magnitude) as discussed earlier.

Conclusions

It is shown that 1*H*-benz[*f*]indene (**1a**), 1*H*-benz[*e*]indene (**2a**), 1*H*-benz[*fg*]acenaphthylene (**3a**) and 1*H*-cyclopenta[*l*]-phenanthrene (**4a**), possessing planar carbon frameworks with a single secondary C(sp^3)H$_2$ center, exhibit modest acidity in the gas phase and in DMSO. The most acidic proton is that bound to the C(sp^3) atom. The origin of their amplified acidity compared to cyclopentane, cyclopentene and cyclopentadiene is the more pronounced anionic resonance, which distributes the negative charge over the whole planar carbon skeleton via mobile π-electrons. It is important to stress, as peculiar as it is, that the anionic resonance is somewhat more effective in the antiaromatic **3a**$^-$ anion than in the aromatic **1a**$^-$ system.

All parent hydrocarbons exhibit tautomerism resulting in a large number of tautomers, some of them possessing a lower stability and correspondingly have a higher acidity. Polycyanation leads to an even larger number of prototropic tautomers with an interesting consequence that the hydrogen walk within the HC(sp^3)–CN grouping leads to the most stable species containing the ketene imine C=C=NH functionality. This simple rule holds for all families of polycyanated compounds. The polycyano derivatives provide hyperstrong superacids championed by **3a$_{CN}$** and **3b$_{CN}$** in the gas phase and in DMSO. The latter is evidenced by the pK_a values of –23.5 and –21.2 (in pK_a units), respectively. It follows that **3a$_{CN}$** and **3b$_{CN}$** are more acidic than the strongest neutral organic superacid identified so far: pentacyanocyclopentadiene (with pK_a = –20.2 in DMSO). They are also stronger acids in DMSO than H_2SO_4 by 25 and 23 orders of magnitude, respectively. The origin of the highly pronounced acidity in multiply cyanated derivatives is identified as a very strong anionic resonance assisted in a concerted way by numerous CN groups, thus being a consequence of the final state. It should be mentioned that there is some evidence that the negative charge demand of the CN group is very low.[65] Our study of substituted methanes and cyclopentadienes shows that NO_2 is a stronger acidifying factor than CN for a singly substituted C(sp^3) carbon atom.[15] However, the triple and pentuple cyanation and nitration of methane and cyclopentadiene, respectively, provides convincing evidence that the CN group is the most suitable substituent in polysubstituted systems, if high acidity is desired. This is due to its very strong cooperative anionic resonance effect and modest steric requirements, which the CN groups combine in an optimal way. It should be noted in passing that a syntagma cooperative effect means that each CN group contributes toward a greater acidity of the polycyano derivative. In the studied 1*H*-benz[*f*]indene, 1*H*-benz[*e*]indene, 1*H*-benz[*fg*]acenaphthylene and 1*H*-cyclopenta[*l*]phenanthrene molecules, polycyanated in a manner that only one hydrogen atom [HC(sp^3)] is left, the anionic resonance stimulated by a large number of CN substituents yields spectacular results irrespective of the aromaticity or antiaromaticity of the corresponding conjugate bases. Their syntheses are, therefore, highly desirable because their interaction with strong (super)bases might lead to a very important phenomenon called spontaneous proton transfer[28,29] and to a wide variety of new compounds. Since the corresponding conjugate bases possess a strongly delocalized and consequently widely dispersed negative charge, they should exhibit a high solubility (e.g. in DMSO and in other solvents of medium polarity and large dielectric constant ε) and a low nucleophilicity. These features guarantee that the produced anions would be relatively inert exhibiting a weak coordinating ability. Their salts might thus provide new superconductive materials and/or other polymeric systems with novel properties.[66,67] It is important to mention that the parent hydrocarbons **1a**,[35–38] **2a**,[39,40] **3a**[41] and **4a**[42,43] have already been synthetized in laboratories.

It is likely that it will be easier to prepare the very stable anions instead of the corresponding acids. However, the recent pioneering success of Richardson and Reed[68] in protonating the $C_5(CN)_5^-$ anion is encouraging, because this is one of the most stable anions we examined so far.[13–15,18] It is noteworthy that the proton was found to be attached exclusively to the nitrogen atom[68] in accordance with our theoretical calculation,[15] which has shown that the acid had a planar heavy atoms structure containing a ketene imine C=C=NH moiety. In other words, $[C_5(CN)_4]C{=}NH$ is an NH and not a CH acid, at least in its most stable form. The same holds for all polycyanated hydrocarbons studied in this work.

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