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Polycyano Derivatives of some Organic Tri- and Hexacyclic Molecules Are Powerful Super- and Hyperacids in the Gas Phase and DMSO: Computational Study by DFT Approach

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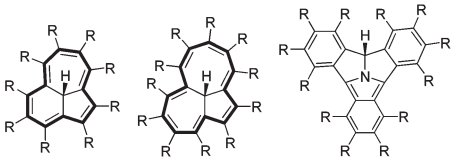

ΔH_{acid} (kcal/mol; R = H)	343.3	346.2	324.3
ΔH_{acid} (kcal/mol; R = CN)	257.2	250.9	$\boxed{\mathbf{242.8}}$
HOMA (R = H)	$(0.175)_{12}$	$\boxed{(\mathbf{0.914})_{\mathbf{14}}}$	

B3LYP/6-311+G(2df,p)//B3LYP/6-31+G(d) calculations convincingly show that tricyclic organic compounds **1** and **2** offer scaffolds suitable for tailoring powerful neutral organic acids. Their cyanation at all $C(sp^2)-H$ positions provide superacids as evidenced by their enthalpies of deprotonation $\Delta H_{\text{acid}}(\mathbf{1b_{CN}}) = 257.2$ and $\Delta H_{\text{acid}}(\mathbf{2b_{CN}}) = 250.9$ kcal mol^{-1}, which are close to the threshold of hyperacidity of 245 kcal mol^{-1}. On the other hand hexacyclic system **3** cyanated at all possible substitution sites along the perimeter except the acidic $C(sp^3)-H$ position provides a true hyperacid with $\Delta H_{\text{acid}}(\mathbf{3a_{CN}}) = 242.8$ kcal mol^{-1}. The reason behind the dramatic acidifying effect is a vigorous anionic resonance effect in the corresponding conjugate bases assisted by a cooperative substituent effect of the CN groups. It is convincingly shown that compounds **1** and **2** represent rigid antiaromatic quasi-[12]annulene and aromatic quasi-[14]annulene *par excellence*, respectively, conforming to Hückel's $(4n + 2)\pi$ electron count rule in the bridged polycyclic systems. Calculations of the pK_a values in DMSO show that the polycyano derivatives are powerful superacids in solutions too.

Introduction

The proton is a small particle that plays a crucial role in many chemical phenomena, being of paramount importance in acid−base chemistry, biochemistry, and molecular biology.[1−3] 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 why these two fundamental properties have been at the focus of intensive interest of a large number of experimental and computational research groups in the past two decades. It should be strongly pointed out that considerable attention has been devoted to the design of powerful neutral organic superacids. They have a number of distinct advantages over their mineral (inorganic) counterparts in solution, being reactive in mild chemical environments and playing an important role in general acid catalysis.[4] Furthermore, very stable anions derived from superacids are useful in olefin polymerization.[5] They also proved useful in the

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stabilization of highly reactive short-lived cations such as HC_{60}^+ and $C_{60}^{\bullet+}$,[6] $C_6H_7^+$,[7] Bu_3Sn^+,[8] and $(Me)_2Cl^+$.[9] Recently, the use of carboranes was pivotal in providing experimental evidence that the proton (H^+) in aqueous solution[10] was neither Eigen ion[11] nor Zundel-type ion[12] but had a $H^+(H_2O)_6$ structure instead. Three main strategies have been developed for this purpose. The first was based on the application of the electronic super-acceptor substituents exemplified by $=NSO_2CF_3$[13,14] or some other acidifying groups,[15−17] whereas in the second approach a concept was proposed of multiple hydrogen bond stabilization of the deprotonation center that greatly enhances the acidity.[18] This is a generalization of the multiple corona effect found in protonated bases[19,20] and single intramolecular or intermolecular corona buttressing effect in some acids.[21,22] The third approach is based on the concept of stabilization of the conjugate bases via a very strong anionic resonance assisted by a large number of cyano substituents.[23−28] The cyano group is a substituent of choice, since it represents the optimal compromise between high electron-withdrawing strength and very modest steric requirements.[28,29] Our study on substituted methanes and cyclopentadienes showed that NO_2 group is a stronger acidifying factor than CN for a singly substituted C(sp^3) carbon atom.[28] However, the triple and pentuple cyanation and nitration of methane and cyclopentadiene, respectively, provide convincing evidence that a CN group is the most suitable substituent in polysubstituted systems if high acidity is desired. The multiple NO_2 substitution leads to strong Coulomb repulsion and pronounced nonplanarities. A particularly interesting class of very "strong yet gentle" superacids is given by carboranes as discussed *in extenso* in several papers by Reed and co-workers[30−33] and in a recent computational study by Koppel and co-workers.[34] In this connection, it should be pointed out that Reed, Wang, Kass and co-workers[35] measured the gas-phase acidity of $H(CHB_{11}Cl_{11})$ carborane yielding $\Delta H_{acid} = 241 \pm 29$ kcal mol^{-1}. The B3LYP/6-311+G(d,p) and G3(MP2) calculations gave for the acidity 237.6 and 238.3 kcal mol^{-1}, respectively, strongly indicating that $H(CHB_{11}Cl_{11})$ is the strongest gas-phase inorganic hyperacid so far.

Design and syntheses of new compounds exhibiting superacidity would be rewarding for several reasons. They would enable formation of new organic cations obtained by protonation of weak bases. A dense ladder of superacids entering the domain of strong superbases[36−41] is desirable, since their mutual interaction would lead to a spontaneous proton transfer in the gas phase[42−44] and formation of new ion pairs[45,46] offering novel molecular systems exhibiting unexpected, interesting, and potentially useful features. Finally, it should be kept in mind that strong acids are irreplaceable reagents in organic syntheses[4,47,48] and in industrial catalysis[49−51] of coal liquefaction, hydrocarbon isomerization, cracking, and alkylations that occur under strongly acidic conditions. In order to overcome the poor reactivity of some starting materials, very strong acidic catalysts and high temperatures have to be used.[52]

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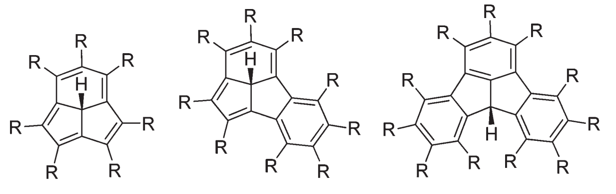
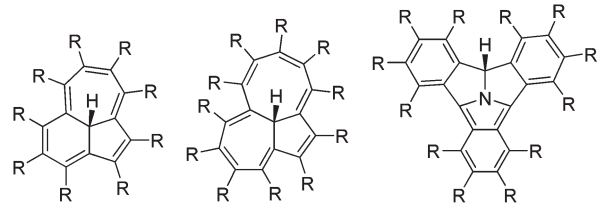


I II III

FIGURE 1. Structure of the tricyclic (**I**) and tetracyclic (**II**) Rees polyenes (R = H) and undecacyanofluoradene (**III**, R = H) and their polycyano derivatives (R = CN).



1 2 3

FIGURE 2. Schematic representation of molecules studied in this work, where R = H or CN, leading to families of tautomers of hydrocarbons and their polycyano derivatives, respectively.

Therefore, building on our previous work, we report here on the results obtained in tailoring new organic acids of very high strength. The starting substrates in designing superacids by our approach are already synthesized and well characterized pure hydrocarbons,[23-27] which provide molecular scaffolds to be dressed by a large number of the electron-withdrawing cyano groups. Our strategy has proved useful in computational prediction of a number of different families of polycyano compounds exhibiting superacidity[23-27] and even hyperacidity as exemplified by cyano derivatives of Rees hydrocarbons[24] (Figure 1). More specifically, the undecacyanofluoradene **III** is the first theoretically predicted neutral organic hyperacid, with the gas-phase deprotonation enthalpy $\Delta H_{\text{acid}}(\textbf{III}) = 246.3$ kcal mol^{-1},[24] within the accuracy of the computational method. The term "hyperacid" has been coined for compounds possessing gas-phase deprotonation enthalpies equal to or below 245 kcal mol^{-1},[24] a value that matches the gas-phase proton affinity of the paradigmatic proton sponge 1,8-bis(dimethylamino)-naphthalene, DMAN,[53] which in turn is widely accepted as the superbasicity threshold.

Here we consider three polycyclic organic compounds **1**−**3** possessing very interesting electronic features (Figure 2), which are related to Rees hydrocarbons **I** and **II** and fluoradene **III** (Figure 1). They will serve as molecular platforms for new powerful neutral organic superacids obtained by polycyanation. It should be stressed that 2*H*-benz[*cd*]azulene, the most stable tautomer of pure hydrocarbon **1** (R = H), has already been synthesized.[54] The same holds for the methyl derivative of **2** attached to the central C(sp^3) carbon atom.[55] The last scaffold **3** has not been prepared as yet, but we feel that it is prone to synthesis (see later). Acidity and geometrical properties of these compounds and their polycyanated derivatives will be examined in the gas phase by the DFT method. Finally, the pK_a values in DMSO will be considered in the framework of the particular polarized continuum model.

Theoretical Methodology

According to Brønsted, acidity is the measure of the capability of a molecule to give up a proton in a chemical reaction. Accordingly, acidity in the gas phase is expressed by eq 1, where GA is the gas-phase acidity (a free-energy term) and DPE is the deprotonation enthalpy (an enthalpy term) for the reaction:

$$\text{AH(g)} \rightarrow \text{A}^-\text{(g)} + \text{H}^+\text{(g)};\ \Delta G_{\text{acid}} = \text{GA};\ \Delta H_{\text{acid}} = \text{DPE} \tag{1}$$

Here AH and A$^-$ denote the acid in question and its deprotonated form, the conjugate base, respectively. ΔG_{acid} gives intrinsic acidity of a compound not influenced by the presence of the solvent molecules or counter-ions. The corresponding deprotonation enthalpy ΔH_{acid} is related to the electronic structure of the acid and its conjugate base and is calculated as:

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

Here, ΔE_{acid} represents the change in the total energy in reaction 1, which includes the electronic and the zero-point energies, as well as the finite temperature (298.15 K) correction, whereas $\Delta(pV)$ denotes the pressure−volume work term. Both ΔG_{acid} and ΔH_{acid} energies are computed and provided, but only the latter will be discussed, since contributions to the Gibbs free energies are practically constant. A theoretical model representing a very good compromise between reliability (accuracy) and practicality (feasibility) is the B3LYP/6-311+G(2df,p)//B3LYP/6-31+G(d) approach. It means that all molecular geometries were optimized and thermodynamic parameters calculated by the very efficient B3LYP/6-31+G(d) method. Analysis of all normal vibrational modes at the same level of theory was used to verify that all structures correspond to true minima on the electronic potential energy surface. The final single-point energy calculations using a highly flexible basis set were performed by the B3LYP/6-311+G(2df,p) scheme in order to describe anions produced by deprotonation. This DFT scheme yields acidities in good agreement with experiment and with more intricate G2 [or G2(MP2)] methods.[56-58] It should be mentioned as a footnote that the choice of B3LYP method was also prompted by its success in reproducing molecular electron affinities.[59-61] All calculations were performed using the Gaussian 03 suite of programs.[62]

Results and Discussion

Molecules studied in this work comprise two tricyclic organic hydrocarbons **1** and **2** and one hexacyclic compound **3**, the latter bearing nitrogen as the central atom (Figure 2).

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TABLE 1. Total Molecular Energies of Studied Molecules in the Gas Phase[a]

molecule	E_{GP}[b]	H_{corr}[b]	G_{corr}[b]	ΔH_{acid}[c]	ΔG_{acid}[c]	E_{DMSO}[b]	$\Delta_r G_{DMSO}$[c]	pK_a
$\mathbf{1a}$	−501.47568	0.19660	0.15243	310.7	303.2	−501.46460	6.8	−0.7
$\mathbf{1b}$	−501.52865	0.19758	0.15361	343.3	335.7	−501.51743	39.2	19.0
$\mathbf{1}^-$	−500.96902	0.18266	0.13902			−501.02467		
$\mathbf{1a_{CN}}$	−1331.81070	0.19732	0.11282	223.7	216.8	−1331.80442	−51.6	−36.1
$\mathbf{1b_{CN}}$	−1331.86545	0.19870	0.11430	257.2	250.3	−1331.85484	−20.9	−17.5
$\mathbf{1c_{CN}}$	−1331.86207	0.19867	0.11456	255.1	248.0	−1331.85157	−23.1	−18.8
$\mathbf{1_{CN}}^-$	−1331.44501	0.18571	0.10268			−1331.46088		
$\mathbf{2a}$	−578.89900	0.23328	0.18428	330.6	322.6	−578.88614	27.4	11.8
$\mathbf{2b}$	−578.92400	0.23350	0.18527	346.2	337.6	−578.91117	42.5	20.9
$\mathbf{2}^-$	−578.36058	0.21941	0.16993			−578.41253		
$\mathbf{2a_{CN}}$	−1593.75019	0.23360	0.13531	241.3	234.1	−1593.73871	−31.8	−24.1
$\mathbf{2b_{CN}}$	−1593.76458	0.23281	0.13448	250.9	243.7	−1593.75255	−22.6	−18.5
$\mathbf{2c_{CN}}$	−1593.76076	0.23280	0.13423	248.5	241.4	−1593.74974	−24.2	−19.5
$\mathbf{2d_{CN}}$	−1593.75378	0.23349	0.13541	243.7	236.3	−1593.73929	−31.5	−23.9
$\mathbf{2e_{CN}}$	−1593.75229	0.23338	0.13524	242.8	235.5	−1593.73689	−32.9	−24.7
$\mathbf{2_{CN}}^-$	−1593.35569	0.22133	0.12394			−1593.36243		
$\mathbf{3a}$	−863.04610	0.29159	0.23513	324.3	316.2	−863.02455	26.5	11.2
$\mathbf{3}^-$	−862.51710	0.27708	0.21999			−862.55159		
$\mathbf{3a_{CN}}$	−1970.15481	0.29198	0.18287	242.8	235.2	−1970.13789	−26.7	−21.0
$\mathbf{3_{CN}}^-$	−1969.75791	0.27964	0.17076			−1969.75268		
$\mathbf{4a}$	−938.15731	0.29490	0.23516	335.5	328.3	−938.14753	36.7	17.4
$\mathbf{4}^-$	−937.60966	0.27958	0.22062			−937.65887		
$\mathbf{4a_{CN}}$	−2045.22980	0.29493	0.18317	244.9	237.4	−2045.21091	−26.3	−20.7
$\mathbf{4_{CN}}^-$	−2044.82829	0.28135	0.17004			−2044.82399		

[a] Obtained at the B3LYP/6-311+G(2df,p)//B3LYP/6-31+G(d) level of theory and in DMSO calculated with the (IPCM)/B3LYP/6-311+G(2d,p)//B3LYP/6-31+G(d) model. H_{corr} and G_{corr} denote thermal correction to enthalpy and Gibbs free energy, respectively, obtained by the B3LYP/6-31+G(d) model. pK_a values in DMSO are calculated using the empirical equation described in the text. [b] In hartree. [c] In kcal mol^{-1}

Their molecular energies and the corresponding gas-phase acidities are given in Table 1. A salient structural feature of compounds **1** and **2** is the central bridging C(sp^3)−H subunit, which brings rigidity into the systems. It "freezes" the [12] and [14]annulene networks, respectively, which are extremely floppy otherwise.

9b*H*-Benz[*cd*]azulenes 1, a Quasi-[12]annulene. The structure of 9b*H*-benz[*cd*]azulene **1a** is an interesting combination of five-, six-, and seven-membered rings bridged by a C(sp^3) tertiary center, thus formally forming an antiaromatic quasi-[12]annulene (Figure 3a). The prototropic tautomerism leads to 13 tautomers in total as shown in Figure 3a, which all but one (**1m**) are more stable than the initial parent structure. They are obtained by the hydrogen walk from the central C(sp^3) site in **1a** to 12 different peripheral C(sp^2) positions. Their relative total electronic energies against the parent compound **1a** are given by the B3LYP/6-31+G(d) method. It appears that they are more stable than the initial system **1a** except for the structures **1l** and **1m**, which are practically degenerate with progenitor **1a**, taking into account the accuracy of the method. The lower energies of **1b**−**1e** tautomers are expected in view of the presence of the benzene moiety, which significantly contributes toward a greater stability of these four systems. Interestingly, it is found that the heptafulvene motif in **1b**, **1f**, **1g**, and **1h** gives rise to increased stability relative to that of **1a** also.

The most stable tautomer in this series, 2*H*-benz[*cd*]azulene **1b**, was synthesized in 1966 by a multistep route based on the carbene-mediated ring expansion of the acenaphthene framework.[54] In this work Boekelheide and Smith noticed also a relative ease of formation of the anion $\mathbf{1}^-$. Previously, Hafner and Schaum had reported the synthesis of 3,4,7,9-tetramethyl derivative of **1b** and observed a higher stability of this product relative to the **1f** tautomer.[63] This topic was recently revived by McGlinchey and co-workers, who found a new method for the preparation of the 2*H*-benz[*cd*]azulene **1b** system and its derivatives.[64] Since the parent compound **1a** is the least stable, its acidity is the highest (ΔH_{acid} = 310.7 kcal mol^{-1}), the tautomer **1m** being an exception. The tautomer **1b** is the most stable in the series, thus defining the upper bound in deprotonation enthalpy given by $\Delta H_{acid}(\mathbf{1b})$ = 343.3 kcal mol^{-1}, implying that it is the least acidic. With this deprotonation enthalpy, molecule **1b** is placed between Rees cyclic polyenes **I** and **II** (R = H) on the acidity ladder, since their deprotonation enthalpies in the gas phase have the values $\Delta H_{acid}(\mathbf{I})$ = 345.6 kcal mol^{-1} and $\Delta H_{acid}(\mathbf{II})$ = 341.3 kcal mol^{-1}.[24] However, as it will become apparent below, polycyano derivative of **1b** is slightly more acidic than both polycyano substituted Rees molecules **I** and **II**.[24]

It is important to point out that the resulting anion $\mathbf{1}^-$ (conjugate base) is the same in all 13 tautomers. It has a planar framework possessing a Hückel aromatic number of 14 π-electrons stabilized by the anionic resonance reflected in 13 Pauling's resonance structures in total. Since all tautomers **1a**−**1m** share the same final conjugate base, the variations in their acidity is determined by their ground state (GS)

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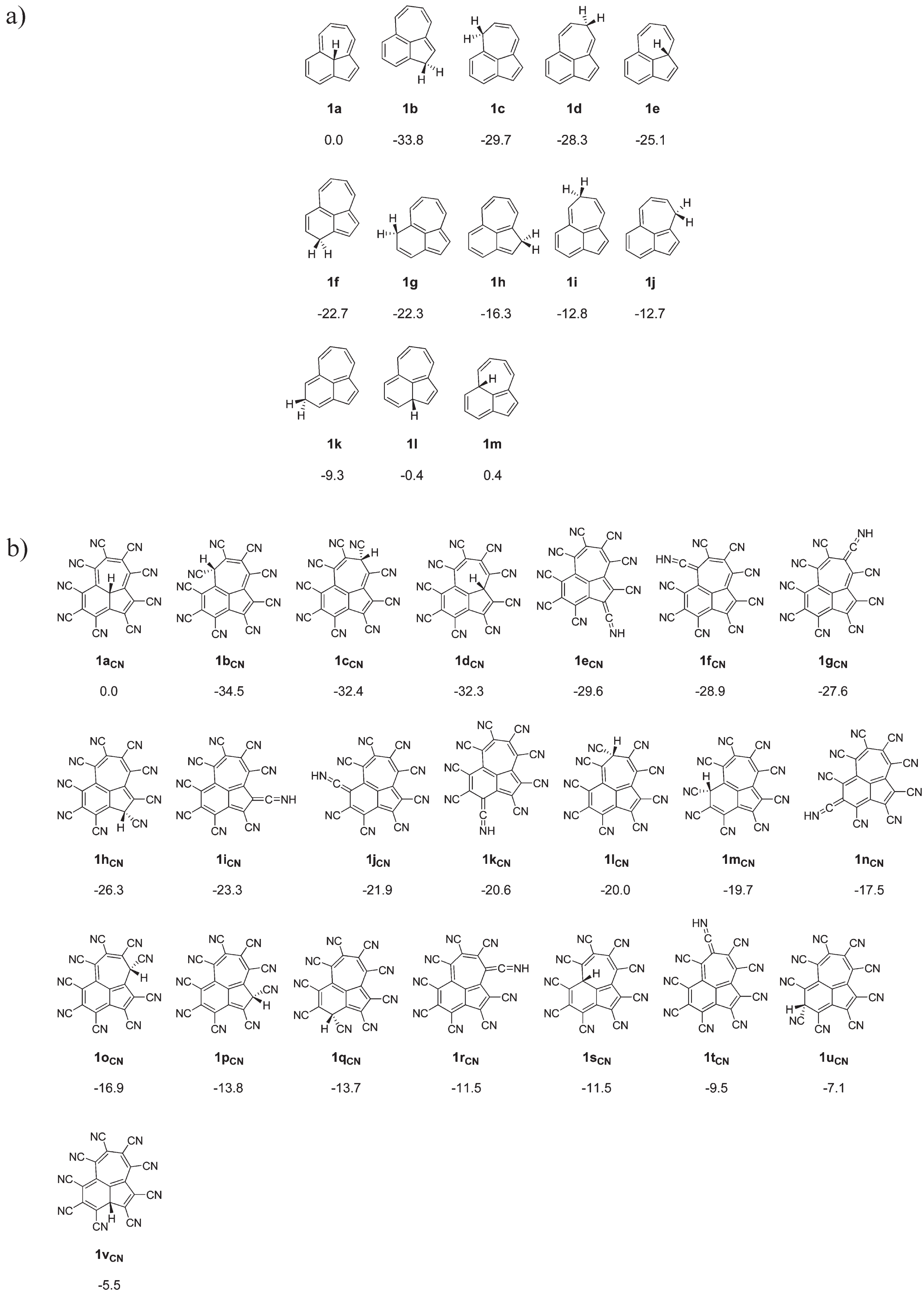

FIGURE 3. (a) Prototropic tautomerism in 9b*H*-benz[*cd*]azulene. The relative stabilities in electronic energies (in kcal mol^{-1}) are calculated by the B3LYP/6-31+G(d) method. (b) Prototropic tautomerism in nonacyano-9b*H*-benz[*cd*]azulene. The relative stabilities in electronic energies are given in kcal mol^{-1} as calculated by the B3LYP/6-31+G(d) method.

energies, i.e., by the initial state properties. This conclusion is general and holds for each family of related molecules examined here, since their conjugate bases are exactly the same. In order to give some idea about the importance of the anionic resonance in $\mathbf{1}^-$, we compare the acidity of **1b** with that of the cyclopentadiene and indene, both deprotonated at the methylene group. The latter are ΔH_{acid}(cyclopentadiene) = 352.6 kcal mol^{-1} and ΔH_{acid}(indene) = 351.8 kcal mol^{-1}.[25] The difference of about 8−9 kcal mol^{-1} makes **1** more acidic than both cyclopentadiene and indene. It is predominantly given by stronger anionic resonance effect in the extended π-framework of **1**.

The 9-fold cyanation of **1a** leads to a derivative $\mathbf{1a_{CN}}$ exhibiting highly pronounced hyperacidity of 223.7 kcal mol^{-1} (Table 1). However, the total number of all possible tautomers of compound $\mathbf{1a_{CN}}$ is 22, which are presented in Figure 3b. It is interesting to observe that the total energies of tautomers $\mathbf{1b_{CN}}$−$\mathbf{1v_{CN}}$ are lower than that of the parent structure $\mathbf{1a_{CN}}$, lying in the range of 5.5−34.5 kcal mol^{-1}. Deprotonation of all tautomers $\mathbf{1a_{CN}}$−$\mathbf{1v_{CN}}$ yields a single conjugate base, which should be very stable as a result of the additional resonance effect between the π-electron charge placed at carbon atoms linked to cyano groups and the terminal nitrogen atom, thus giving rise to a C═C═N$^-$ distribution of the π-electrons. Thus, the cyano groups enable a considerably better accommodation (dispersion) of the negative charge in the anion. This is an important feature, which leads to a low nucleophilicity of the conjugate bases. An interesting finding worth of mentioning is given by the fact that polycyano hydrocarbon derivatives often undergo prototropic tautomerism, as for example in pentacyanocyclopentadiene,[28] where the most stable structure of neutral acid possess keteneimine C═C═NH moiety, instead of the HC(sp^3)−CN structural fragment. This theoretical prediction was confirmed by a parallel experimental investigation of Richardson and Reed,[65] who found that a very stable planar $C_5(CN)_5^-$ anion could be protonated only at the nitrogen atom, yielding a fulvene-like structure. Protonation at the carbon atom of the five-membered ring, which would give a cyclopentadiene molecular architecture instead, was not observed. The latter finding was corroborated by a subsequent *ab initio* study by Schaefer and co-workers.[66] It follows that pentacyanocyclopentadiene is a nitrogen acid instead of a carbon one.

The most stable structure, $\mathbf{1b_{CN}}$, exhibits superacidic properties as reflected by $\Delta H_{acid}(\mathbf{1b_{CN}})$ = 257.2 kcal mol^{-1}. To put this result in perspective, it is useful to compare it with the gas-phase acidity of perchloric acid, $\Delta H_{acid}(HClO_4)$ = 299.9 ± 5.7 kcal mol^{-1} as recently determined experimentally[67] and calculated earlier by using composite G3 methodology to yield $\Delta H_{acid}(HClO_4)$ = 299.2 kcal mol^{-1}.[68] This was the reason why 300 kcal mol^{-1} was selected as a threshold of superacidity in the gas phase.[68] It turns out that molecule $\mathbf{1b_{CN}}$ is around 31 orders of magnitude stronger an acid than $HClO_4$ in the gas phase, which is remarkable indeed. It should be emphasized that $\mathbf{1b_{CN}}$ defines the lower bound in acidity of these systems, meaning that all the remaining tautomers are even more acidic. We also note in passing that $\mathbf{1b_{CN}}$ is somewhat stronger an acid than the most stable tautomers of polycyanated Rees compounds, namely, of the heptacyano derivative of **I** (ΔH_{acid} = 261.8 kcal mol^{-1}) and of the nonacyano derivative of **II** (ΔH_{acid} = 259.0 kcal mol^{-1}).[24] It is interesting to note that the prototropic tautomers involving keteneimine C═C═NH moiety are less stable than their HC(sp^3)−CN counterparts, if attached to the seven-membered ring. This is in contrast with a rule stating that C═C═NH fragment is the most acidic part in polycyclic compounds possessing five- and six-membered annelated rings as discussed here and in previous work.[23−28] It should be pointed out that the eight-membered ring gives rise to the same exception (see below). Since the parent **1a** molecule is already prepared, its polycyanation would provide one of the most powerful organic superacids considered so far by computational methods.

Tricyclic Quasi-[14]annulenes 2. One of the simplest extensions of system **1** pertaining to larger π-systems would be compound **2a**. This interesting system is a modified quasi-[14]annulene encompassing the five-, seven-, and eight-membered polyene rings surrounding the central tertiary C(sp^3)−H center (Figure 4a). A derivative of the parent molecule **2a**, having a methyl group instead of a hydrogen atom attached to the central sp^3 carbon atom, was prepared by Müllen in the mid-1980s.[55]

The neutral C(sp^3)H acid **2a** exhibits prototropic tautomerism resulting in 15 tautomers. Unlike molecule **1a**, where all remaining tautomers were more stable than the parent system, there are here only three tautomers lower in energy than **2a**. This is not surprising, because there is no classical aromatic substructure in any of the tautomers **2b**−**2o**. However, structures **2b**, **2c** and **2d** are more stable than **2a** by 16.2, 9.8, and 9.0 kcal mol^{-1}, respectively, at the B3LYP/6-31+G(d) level of theory. Others like **2e**, **2f**, and **2g** are slightly less stable than the bridged quasi-[14]annulene **2a**. Acidities of **2a** and **2b** are given by $\Delta H_{acid}(\mathbf{2a})$ = 330.6 kcal mol^{-1} and $\Delta H_{acid}(\mathbf{2b})$ = 346.2 kcal mol^{-1}, the latter value representing the upper bound. The acidity of the most stable tautomer **2b** is 3 kcal mol^{-1} lower compared to the corresponding **1b** compound.

Undecacyano derivatives, encompassing systems completely substituted at the molecular perimeter, are large in number. There are altogether 26 prototropic tautomers, but with just 4 systems more stable than $\mathbf{2a_{CN}}$. They are depicted together with the tricyclic quasi-[14]annulene structure $\mathbf{2a_{CN}}$ in Figure 4b. Structures and relative stabilities of the remaining tautomers are deposited in the Supporting Information. Two most stable tautomers $\mathbf{2b_{CN}}$ and $\mathbf{2c_{CN}}$ possess a keteneimine fragment attached to the five-membered ring. On the contrary, in prototropic tautomers $\mathbf{2d_{CN}}$ and $\mathbf{2e_{CN}}$ there is an inversion in the stability of the HC(sp^2)−CN and C═C═NH fragments within the eight-membered ring, the former being energetically more favorable.

These tautomers are all nonplanar as a result of steric repulsions between the cyano groups. The ΔH_{acid} values for $\mathbf{2a_{CN}}$ and $\mathbf{2b_{CN}}$ are 241.3 and 250.9 kcal mol^{-1}, respectively, which means that all undecacyano derivatives of tricyclic quasi-[14]annulene are strongly acidic satisfying inequality $\Delta H_{acid} \leq 250.9$ kcal mol^{-1}. It is interesting to observe that although the unsubstituted compound **2b** was by 3 kcal mol^{-1} less acidic than **1b**, its polycyanated derivative $\mathbf{2b_{CN}}$ is by 6.3 kcal mol^{-1} a stronger acid in the gas phase than $\mathbf{1b_{CN}}$

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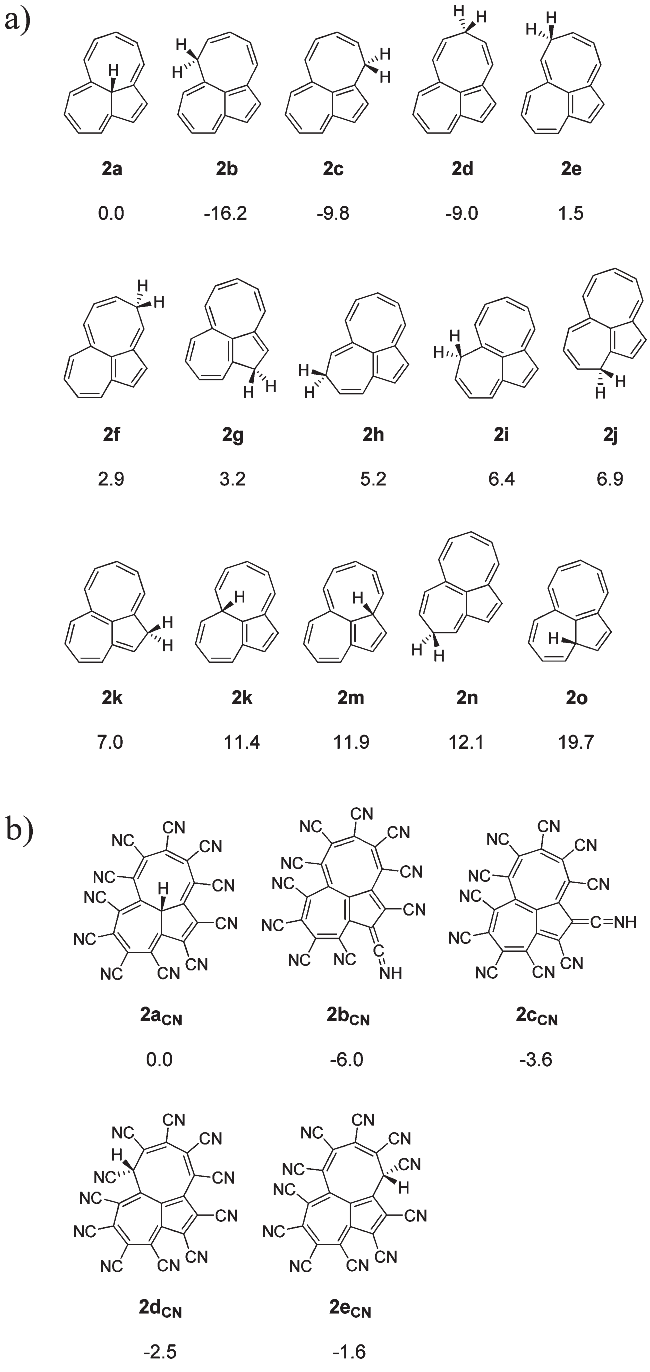


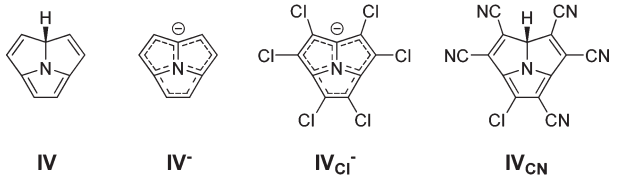
FIGURE 4. (a) Prototropic tautomerism in tricyclic-[14]annulene. The relative stabilities in electronic energies (in kcal mol^{-1}) as calculated by the B3LYP/6-31+G(d) method. (b) Prototropic tautomerism in undecacyano-tricyclic-[14]annulene. The relative stabilities in electronic energies (in kcal mol^{-1}) are calculated by the B3LYP/6-31+G(d) method.

coming close to the 250 kcal mol^{-1} borderline. One of the reasons for that is a very strong anionic resonance effect in the deprotonated form $\mathbf{2b_{CN}}^{-}$, which is efficiently assisted by 11 cyano groups compared to 9 cyano groups occurring in $\mathbf{1b_{CN}}^{-}$. It should be stressed that the anionic resonance is very strong despite the formally antiaromatic number of the 16 π-electrons in $\mathbf{2b_{CN}}^{-}$. This is in accordance with our earlier findings that anionic resonance is a stronger stabilization factor than aromaticity and that it is effective in antiaromatic systems too.[24,25,27]

Hexacyclic Compound 3. Incorporation of the nitrogen atom instead of the central carbon atom in fluoradene allows for the formation of a very symmetrical hexacyclic molecule **3a** (Figure 5a), which has one strongly acidic C(sp^3)−H center. This acidic hydrogen atom can walk around the perimeter of the molecule, creating in total four possible tautomers. They are shown in Figure 5a.

It should be pointed out that compound **3a** represents a tribenzo derivative of tricyclic azaacepentalene **IV** (Scheme 1), recently prepared by Mascal and Cerón Bertran[69] by N-oxidation of azatriquinacene followed by treatment with a base. This work was inspired by de Meijere's landmark synthesis of the triquinacene dianion.[70,71] In addition, azaacepentalenide anion $\mathbf{IV}^{-}$ as well as its perchloro derivative $\mathbf{IV_{Cl}}^{-}$ were synthesized.[69] We have calculated deprotonation enthalpies of compound **IV** and its hexacyano derivative $\mathbf{IV_{CN}}$ to be 335.6 and 255.1 kcal mol^{-1}, respectively, as obtained by the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) method.[26] The former value agrees with Mascal's computational result of 333.5 kcal mol^{-1} obtained by using the B3LYP/6-311++G(d,p) approach.[72]

SCHEME 1



It is noteworthy that the parent tautomer **3a** is by far more stable than all of the remaining tautomers. This is a consequence of the fact that tautomers **3b**−**3d** have one aromatic benzene moiety less than the parent compound. It appears that **3b** and **3c** are less stable than **3a** by some 20−22 kcal mol^{-1}, being thus in harmony with our estimate of the aromatic stabilization of the free benzene, determined to be around 22.6−23.8 kcal mol^{-1},[73] which is in a good agreement with the experimental estimate of 21.6 ± 1.5 kcal mol^{-1}.[74] Tautomer **3d** is less stable by 31 kcal mol^{-1} because of an additional pyramidalization and more pronounced nonplanarity in the neutral form. It is, therefore, sufficient to examine the acidity of the **3a** molecule. The B3LYP model employed here gives $\Delta H_{acid}(\mathbf{3a})$ = 324.3 kcal mol^{-1}, revealing that **3a** is the strongest unsubstituted acid examined in this work. It is of interest to put this result into perspective by comparison with some known Brønsted mineral acids. For instance, molecule **3a** is close in its acid strength to $MeSO_3H$ and HNO_3, whose experimentally determined gas-phase deprotonation enthalpies are 320.9 ± 2.2[13] and 324.5 ± 0.2 kcal mol^{-1},[75] respectively.

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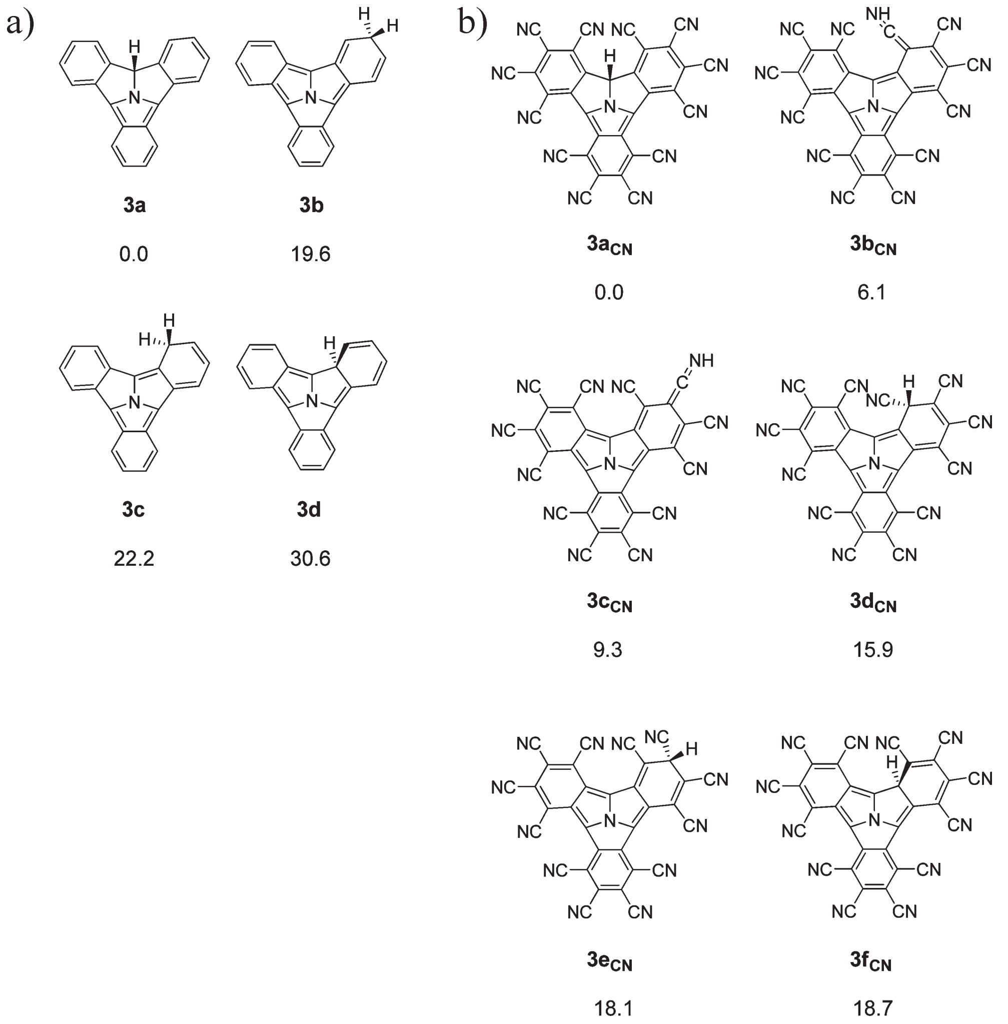

FIGURE 5. (a) Prototropic tautomerism in hexacyclic compound **3**. The relative stabilities in electronic energies (in kcal mol^{-1}) are calculated by the B3LYP/6-31+G(d) method. (b) Prototropic tautomerism in dodecacyano derivative of the hexacyclic compound **3**. The relative stabilities in electronic energies (in kcal mol^{-1}) are calculated by the B3LYP/6-31+G(d) method.

Further, **3a** is a much more potent acid than both unsubstituted Rees hydrocarbons **I** and **II** (ΔH_{acid}(**I**) = 345.6 kcal mol^{-1} and ΔH_{acid}(**II**) = 341.3 kcal mol^{-1})[24] as well as unsubstituted fluoradene molecule **III** (ΔH_{acid}(**III**) = 330.3 kcal mol^{-1}),[24] which had served as a molecular skeleton for its hyperacidic undecacyano derivative.[24]

Dodecacyano derivative of **3a** has a total of 6 prototropic tautomers displayed in Figure 5b. Derivative **3a**$_{\mathbf{CN}}$ is again the most stable tautomer as a result of the presence of three fused benzene moieties. Interestingly, the cyanation did not change much the relative stability of tautomers, although polycyanation introduced significant nonplanarities induced by congested CN groups. It is intuitively expected that **3a**$_{\mathbf{CN}}$ is the most acidic compound considered here for two reasons: (1) the parent compound **3a** is already more acidic than fluoradene (**III**) for R = H, and (2) it has an additional CN group compared to polycyanofluoradene (R = CN) in Figure 1. Indeed, its deprotonation enthalpy is ΔH_{acid}(**3a**$_{\mathbf{CN}}$) = 242.8 kcal mol^{-1}, which is by 14.4 and 8.1 kcal mol^{-1} lower than in **1b**$_{\mathbf{CN}}$ and **2b**$_{\mathbf{CN}}$, respectively, implying that its acidity is higher. Most importantly, it follows that molecule **3a**$_{\mathbf{CN}}$ is a true neutral organic hyperacid, since its deprotonation enthalpy is below the hyperacidity threshold[24] of 245 kcal mol^{-1}. It is just 2 kcal mol^{-1} less acidic that the experimentally measured value for H(CHB$_{11}$Cl$_{11}$).[35] It is worth pointing out that **3a**$_{\mathbf{CN}}$ is by 47 orders of magnitude stronger an acid than sulfuric acid in the gas phase.

Recently,[76] it was demonstrated that oxidation of a tertiary nitrogen atom yielding an amine-*N*-oxide group ($R_3N^+{-}O^-$) in the vicinity of a deprotonation center amplifies the acidity around 9−17 kcal mol^{-1} in the gas phase. Therefore, it is of some interest to apply the same principle to molecules **3** and **3**$_{\mathbf{CN}}$ in an attempt to design even more potent superacids. It should be mentioned that such oxidation of tertiary amines is readily performed with hydrogen peroxide or peroxy acids and that it serves as a convenient protective group for amino or imino nitrogen in synthetic work.[77] Formation of an *N*-oxide group at the central position of molecule **3** produces the same number of tautomers in **4** and in its polycyanated derivative **4**$_{\mathbf{CN}}$ compared to parent compound with practically identical relative stabilities of tautomers as presented in Figure 5a and b. Therefore, we will comment only on the acidity of the most stable

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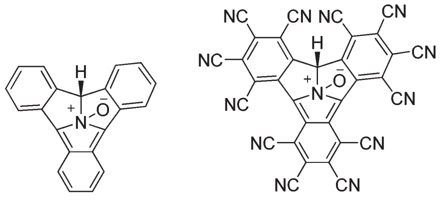

4a **4a$_{CN}$**

FIGURE 6. Most stable tautomers of an *N*-oxide derivative of hexacyclic molecule **3** in its unsubstituted (**4a**) and polycyano (**4a$_{CN}$**) forms.

tautomers of such *N*-oxide derivatives **4a** and **4a$_{CN}$** displayed in Figure 6.

The gas-phase acidity parameters of these two molecules are presented in Table 1. It turned out that oxidation of the central amino nitrogen into an *N*-oxide group did not result in any acidity enhancement. On the contrary, acidities of molecule **4a** and **4a$_{CN}$** are by 11.2 and 2.1 kcal mol^{-1} lower than the corresponding **3a** and **3a$_{CN}$** molecules, respectively. Nevertheless, **4a** and **4a$_{CN}$** would provide interesting new members on the ladder of organic super/hyper-acids once synthesized.

Acidities in DMSO. All acid-catalyzed processes of industrial and academic relevance by definition involve a proton transfer between ionizable group of an acid and the substrate occurring in solution. Therefore, the knowledge of the pK_a values of acids involved in chemical transformations is of paramount importance for a deeper understanding of their mechanism and a rational modification of the key steps. Unfortunately, the experimental determination of pK_a's of various organic acids in different solvents is not an easy task. It is difficult and seldom possible to measure the pK_a of given acidic hydrogen with the necessary accuracy,[78-80] particularly for very strong and very weak acids. For example, in water solutions acids with pK_a values lesser than that of the hydronium ion (H_3O^+), with pK_a = −1.74,[81] cannot be measured and alternative methods for their estimation are required. Consequently, theoretically predicted pK_a values for very strong acids considered here might be helpful for the experimental work.

The solvent of choice was dimethyl sulfoxide (DMSO) for several reasons. It enables measurements of the pK_a constants free of ion associations,[82] and it is widely used in chemistry and chemical technology because of favorable features related to its aprotic, dipolar, and protophilic characteristics and relatively high dielectric constant (ε = 46.7). As a consequence, an enormous number of the experimental pK_a values in DMSO are available nowadays, which have been provided mostly by Bordwell and Taft and their co-workers[82-85] as well as some other researchers.[86-88] Thus, it comes as no surprise that acidity constants of organic molecules in DMSO were also a challenge for computational modeling in the past.[89-94] However, the accurate computation of the solution−phase acid dissociation constants is far from being a trivial task even for small molecules. As such, a number of computational procedures have recently been devised for this purpose with variable success. Since it is impossible to give a complete overview of these models, we refer only to several excellent review articles that recently appeared in this lively research field.[95-101] The approach we used[102] is briefly described below.

The total change in the free energy for the deprotonation reaction in DMSO is of the form

$$\mathrm{AH(solv)} + \mathrm{DMSO(solv)} \rightarrow \mathrm{A^-\,(solv)} + \mathrm{DMSOH^+(solv)};\ \Delta_r G_{\mathrm{DMSO}} \qquad (3)$$

In our current work on the acidity in DMSO solutions,[102] we used eq 3 as the origin of the computational treatment, where all species were considered first in the gas phase. Their geometries and zero-point vibrational frequencies were determined by the B3LYP/6-31+G(d) method. The total electronic energies in the gas phase were computed subsequently at the single-point B3LYP/6-311+G(2d,p) level. Then the free energies of the deprotonation reaction $\Delta_r G_{\mathrm{DMSO}}$ were estimated by eq 4:

$$\begin{aligned}\Delta_r G_{\mathrm{DMSO}} = {} & \Delta_r G_{\mathrm{GP}} + \Delta G_{\mathrm{DMSO}}(\mathrm{A^-}) + \Delta G_{\mathrm{DMSO}}(\mathrm{DMSOH^+}) \\ & - \Delta G_{\mathrm{DMSO}}(\mathrm{AH}) - \Delta G_{\mathrm{DMSO}}(\mathrm{DMSO}) \qquad (4)\end{aligned}$$

In calculating solvation energies the isodensity polarized continuum model (IPCM) was used[103,104] and the isodensity frontier molecular surfaces of 0.0004 e B^{-3} have been employed based on the (IPCM)/B3LYP/6-311+G(2d,p)//B3LYP/6-31+G(d) method. The obtained $\Delta_r G_{\mathrm{DMSO}}$ values were then correlated with the experimentally determined DMSO pK_a values for 326 widely different acids. The latter were taken from collections of data provided by Bordwell[83] and Reich.[105] A very good correlation was obtained as

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evidenced by regression parameters $R^2 = 0.972$ for correlation coefficient, $\Delta_{abs}(pK_a) = 1.0$ unit for the overall standard absolute deviation, and the maximal standard absolute deviation of $\Delta_{abs,max}(pK_a) = 2.5$ unit.[102] This is to our knowledge the best empirical correlation obtained for such a large group of markedly different acids covering a well-spread range of pK_a values between 1.6 and 59.0 units. The final equation reads

$$pK_a(AH)_{DMSO}{}^{theor} = 0.606\Delta_r G(AH)_{DMSO} - 4.8 \qquad (5)$$

Equation 5 is applied in the present work to estimate the acidity constants of the most stable tautomers of acids. Values of $\Delta_r G_{DMSO}$ energies and the predicted pK_a values in DMSO are given in Table 1. The resulting $\Delta_r G_{DMSO}$ free energies are negative for polycyano derivatives, meaning that the proton transfer to the solvent DMSO molecules is strongly favored in these cases. The pK_a values for the parent hydrocarbons **1b**, **2b**, **3a**, and **4a** are 19.0, 20.9, 11.2, and 17.4, respectively. These results are not surprising, because pK_a values perfectly parallel the corresponding gas-phase deprotonation enthalpies, meaning that stronger acid in the gas phase possesses a lower pK_a value in DMSO. Thus, the compound **3a** is again the most acidic unsubstituted parent molecule with pK_a value of 11.2. To put this result into perspective, it is useful to mention that DMSO acidity of **3a** is in between the pK_a values of HCN (12.9)[83] and HNO_2 (7.5).[83] It is interesting to observe that the difference in acidity between molecules **1b** and **3a** is 14.3 pK_a units in the gas phase but only 7.8 pK_a units in DMSO, implying that the latter is more acidic in both phases, albeit to a much lesser extent in solution. This attenuation of the acidity is due to the larger molecular volume of compound **3a** relative to **1b**, thus being in harmony with an early observation of Taft and Bordwell,[84] 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 acidity of the most stable polycyano derivatives $\mathbf{1b_{CN}}$, $\mathbf{2b_{CN}}$, $\mathbf{3a_{CN}}$, and $\mathbf{4a_{CN}}$. Their pK_a values are −17.5, −18.5, −21.0, and −20.7, respectively. It follows that polycyano derivatives examined here are superstrong acids both in the gas phase and in DMSO. It is noteworthy that the most acidic system is provided by the hexacyclic scaffold **3a** in its polycyanated $\mathbf{3a_{CN}}$ form. Possessing a pK_a value of −21.0, it is even more potent neutral organic superacid than pentacyanocyclopentadiene, which was calculated to have $pK_a = -20.2$ in DMSO,[25] but significantly less acidic than compound $\mathbf{IV_{CN}}$ (Scheme 1) with pK_a of −26.5.[26] This is again a consequence of the size of the molecular system. It is of interest to compare these values with the pK_a value of H_2SO_4 in DMSO, considered by Gillespie and Peel[106] as a reference superacid. Since the experimental $pK_a(H_2SO_4)_{DMSO} = 1.99$,[83] it follows that compound $\mathbf{3a_{CN}}$ is around 23 orders of magnitude stronger an acid in DMSO than H_2SO_4, which is a remarkable finding. The corresponding difference in the gas phase was larger (47 orders of magnitude) as discussed above.

Geometrical Parameters and Aromaticity. It is of considerable interest to discuss the alleged anti/aromatic character of molecules **1a** and **2a** and the anionic resonance in the corresponding conjugate bases. The neutral acids possess rigid structures with potential [12] and [14]annulene distribution of the π-electrons over the CC perimeters. This is an important feature, because genuine monocyclic higher annulenes are nonplanar due to angular strain and/or repulsion of the inner H atoms, let alone antiaromaticity as in [12]annulene.[107,108] Consequently, they are floppy, thus making aromatic stabilization impossible[109−111] as for example in [14]annulene. Annulene chemistry undergoes a renaissance in recent years.[112] The reason behind is the rapid development of new synthetic routes to annulenes[113] allowing easy functionalization of the hydrocarbon backbone toward macrocycles and a recognition of prospective applications of these π-electron rich systems as novel materials.

Recently,[114] we have demonstrated that Rees compound **I** is a quasi-[10]annulene, since it possesses strong π-electron delocalization over the CC perimeter. Its aromatic character was determined to be 83% employing the geometric HOMA (harmonic oscillator model of aromaticity) criterion, proposed by Krygowski and co-workers.[115] Calculations of HOMA indices are based on the following formula:

$$(\mathrm{HOMA})_n = 1 - \left[\frac{\alpha(6)}{n}\right]\sum_{i=1}^{n}(d(\mathrm{CC})_{\mathrm{opt}} - d(\mathrm{CC})_i)^2 \qquad (6)$$

where the summation is extended over all n bonds of the investigated cyclic fragment, and α(6) is a free parameter determined so that HOMA = 0 for a reference nonaromatic completely localized system like, e.g., the Kekule's structure of benzene. In that case α(6) is 257.7. It turns out that HOMA is dimensionless quantity assuming 1 for a perfectly aromatic system without alternation of bond distances, implying that all C−C bond distances are equal to the optimal distance d_{opt}. The latter takes a value of 1.388 Å, which is close to the true bond distance in the equilibrium D_{6h} structure of benzene taken as a paradigmatic aromatic molecule. B3LYP/6-31+G(d) results yielded $(0.828)_{10}$ as HOMA parameter of molecule **I**. In contrast, molecule **II** turned out to be less convenient model for quasi-[14]annulene, since its HOMA = $(0.702)_{14}$. This is a consequence of the fact that the perimeter network of the potentially aromatic 14 π-electrons in **II** has two competitive local aromatic sub-patterns involving 10π and 6π electrons. Consequently, the π-electron delocalization over the molecular rim is incomplete, and the aromaticity is diminished.

In evaluating the aromatic character of tricyclic annulenes **1a** and **2a** and their deprotonated forms we used here the B3LYP/6-31+G(d) optimized structures. Relevant geometrical parameters and Löwdin π-bond orders[116] are graphically depicted

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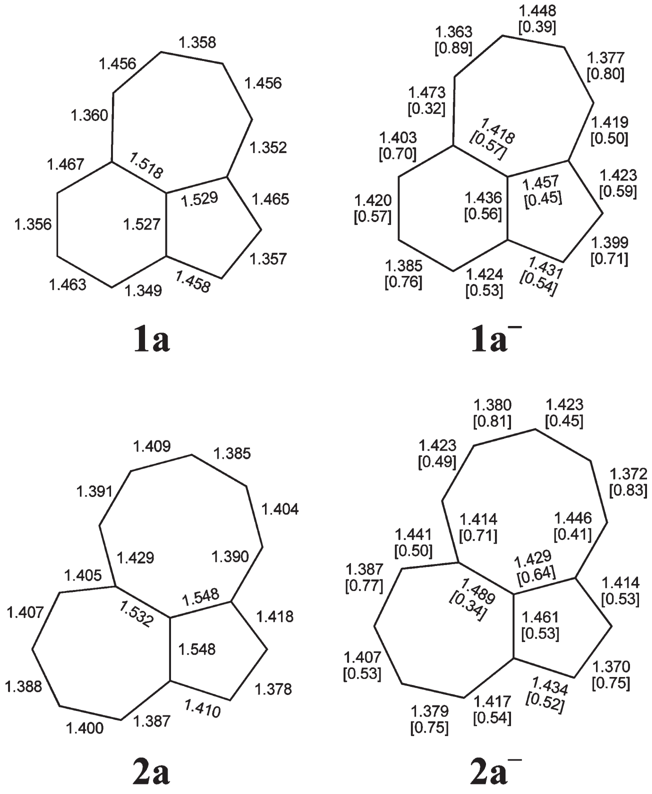

1a **1a⁻**

2a **2a⁻**

FIGURE 7. Structural parameters (in Å) and relevant Löwdin π-bond orders [HF/6-31G(d)//B3LYP/6-31+G(d) level of theory, in |e|] for molecules **1a** and **2a** and their anions.

in Figure 7, whereas the corresponding HOMA parameters are presented in Figure 8.

Inspection of data presented in Figure 7 reveals that the "frozen" quasi-[12]annulene **1a** possesses strongly localized distribution of C−C bonds around the perimeter, in agreement with an antiaromatic number of π-electrons. All 12 C−C bonds fall in a rather wide range between 1.349 and 1.467 Å. The localized nature of the structure of **1a** molecule was also observed in the crystal structure of this system, which revealed bond alternation over the perimeter and inside constituting monocyclic fragments.[64] This feature is further evidenced through the corresponding HOMA parameters displayed in Figure 8. The HOMA index corresponding to delocalization over the rim is HOMA(**1a**) = $(0.175)_{12}$, which suggests that compound **1a** exhibits a low aromatic character of only 18% over the perimeter. Obviously, the π-system in **1a** is highly localized. This is in accordance with previous ^{1}H NMR measurements, which showed that **1a** displayed a pronounced paratropicity. These findings support a conclusion of Hafner and Schaum[63] that **1a** is antiaromatic quasi-[12]annulene *par excellence*. The deprotonated system **1**$^-$ has an aromatic number of 14 π-electrons. Nevertheless, its bond distances reflect significant bond alternation, albeit to a lesser extent compared to the neutral molecule. It is a planar system with bond orders within the range 0.32−0.89. Despite large disparities, delocalization of the π-electrons is considerable. This is supported by HOMA values, which are all substantially increased upon deprotonation. Their pattern reveals that various π-electron substructures are tending to maximize its aromaticity and minimize antiaromaticity. All of these rings compete for the aromatic number of π-electrons, and none of them is able to ensure the ideal $(4n + 2)\pi$ number due to a presence of the adjacent fused rings, which try to be aromatic themselves. The final π-electron distribution is a result of the interplay between these competing tendencies. It turns out that the excess negative charge in **1**$^-$ resides mostly in the six-membered ring as evidenced by the HOMA value $(0.753)_6$. Taken all together, one can conclude that molecule **1**$^-$ does not represent a good model for the aromatic quasi-[14]annulene. Nevertheless, it is strongly stabilized through anionic resonance effect.

The very interesting bridged quasi-[14]annulene **2a** displays a rather weak bond alternation over its perimeter. It appears that all 14 C−C bonds fall in a closely spaced range between 1.378 and 1.418 Å. As a result, the HOMA value for the perimeter π-electron distribution is very high with the value HOMA(**2a**) = $(0.914)_{14}$. It suggests that the π-electron ring structure over the **2a** rim is aromatic by almost 92%. This qualifies molecule **2a** for a quasi-[14]annulene. For the sake of comparison the benzene molecule in its D_{6h} structure has a HOMA index of $(0.969)_6$ at the same B3LYP/6-31+G-(d) level of theory with all six C−C bonds assuming a value of 1.399 Å. It follows that the aromaticity of **2a** over its perimeter is just a bit shy of the aromaticity in benzene.

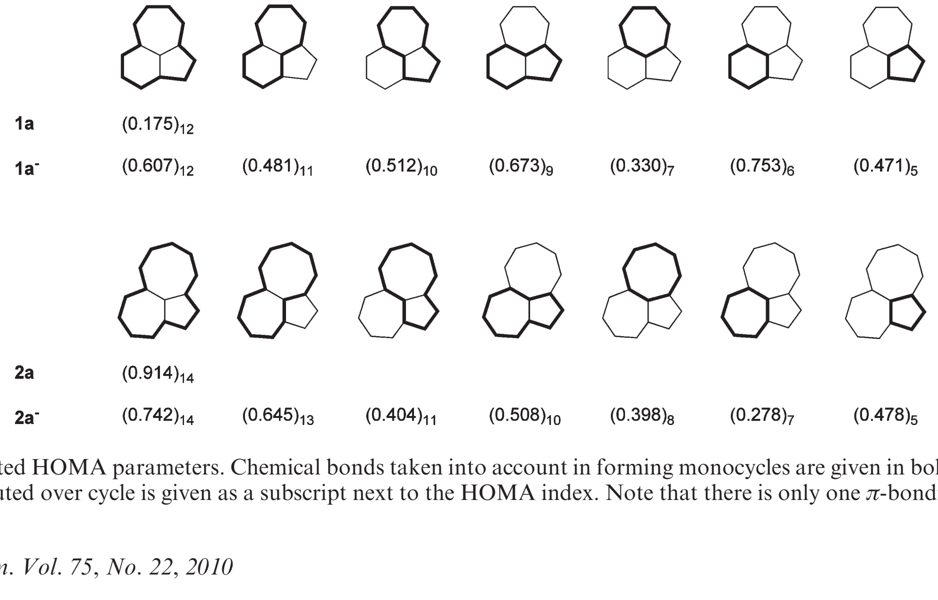

FIGURE 8. Calculated HOMA parameters. Chemical bonds taken into account in forming monocycles are given in bold, and the number of π-electrons n distributed over cycle is given as a subscript next to the HOMA index. Note that there is only one π-bonding pattern in neutral molecules.

Deprotonation of **2a** yields planar $\mathbf{2}^-$ anion, which in turn has an antiaromatic number of 16 π-electrons. This resulted in a larger bond fixation in $\mathbf{2}^-$as evidenced by the spread of relevant bond distances over the perimeter in a range between 1.370 and 1.441 Å, which is significantly larger than in **2a**. It is again a consequence of the competition of different π-electron pathways. They have high participation in overall delocalization as evidenced by large HOMA values for pathways n = 5, 10, and 13 (Figure 8). They are indicative of a strong anionic resonance stabilization despite the antiaromatic number of the π-electrons. We note in passing that the analogous analysis performed for polycyanated derivatives $\mathbf{1a_{CN}}$ and $\mathbf{2a_{CN}}$ yields the same conclusions and very similar trends in the HOMA values, with a distinct difference that the corresponding HOMA values are significantly reduced because of a strong electron-withdrawing effect of the cyano groups and their stabilizing resonance effect with the carbon π-network. The latter is particularly strong in the corresponding anions.

In wrapping up this section, it is fair to conclude that molecule **2a**, kept rigid by the central tetra-coordinated $C(sp^3)-H$ fragment represents a quasi-[14]annulene. On the other hand, **1a** is indeed an antiaromatic compound as conjectured by Hafner and Schaum.[63]

Concluding Remarks

It is shown by B3LYP/6-311+G(2df,p)//B3LYP/6-31+G(d) calculations that tricyclic molecules **1** and **2**, as well as hexacyclic system **3**, all possessing an acidic $C(sp^3)-H$ center, provide scaffolds for very strong superacids (**1** and **2**) or a hyperacid (**3**) in the gas phase, if polycyanated at available $C(sp^2)$ positions. The hydrogen walk around molecular perimeter provides a large number of tautomers in each family of molecules. Considering the most stable tautomers in pure hydrocarbon systems **1**−**3**, one finds out that they are moderately acidic as evidenced by ΔH_{acid} values of 343.3, 346.2, and 324.2 kcal mol^{-1}, respectively. Dramatic enhancement in acidity is obtained by polycyanation yielding $\Delta H_{\mathrm{acid}}(\mathbf{1b_{CN}})$ = 257.2, $\Delta H_{\mathrm{acid}}(\mathbf{2b_{CN}})$ = 250.9 and $\Delta H_{\mathrm{acid}}(\mathbf{3a_{CN}})$ = 242.8 in kcal mol^{-1}, implying that $\mathbf{1b_{CN}}$ and $\mathbf{2b_{CN}}$ are highly superacidic systems approaching the hyperacidity threshold of 245 kcal mol^{-1}, which in turn coincides with the gas-phase proton affinity of the 1,8-bis(dimethylamino)-naphthalene (DMAN).[24] On the other hand, the $\mathbf{3a_{CN}}$ ΔH_{acid} value is below this threshold, meaning that it is the first true neutral organic hyperacid in the gas phase tailored by computer up to now. To put its acid strength in perspective, one should emphasize that it is a stronger an acid than H_2SO_4 by 47 orders of magnitude in the gas phase. The origin of the highly pronounced acidity of these molecules is identified as a very strong anionic delocalization of the excess negative charge in the corresponding conjugate bases, which is vigorously amplified by concerted action of multiple CN substituents. The anionic resonance is effective in both aromatic and antiaromatic monoanion systems, indicating a tremendous power of the anionic resonance. It should be stressed that deprotonation energies of the systems studied in this work deeply enter the ladder of superbases, to mention only the proton affinity PA = 270.6 kcal mol^{-1} of the bis-guanidino compound $H_2C\{hpp\}_2$ synthesized recently[41] (hppH = 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine). The interaction of strong superacids and superbases once prepared would lead to a large number of weakly coordinated ion pairs with interesting properties. It is important to underline that polycyano derivatives are potent superacids in DMSO, as illustrated for example by $\mathbf{3a_{CN}}$ system, which is stronger an acid than H_2SO_4 in DMSO by 23 orders of magnitude.

It is important to note that the chemistry of the cyano group is known.[117−119] Concomitantly, we believe that synthesis of a number of predicted superacids is feasible, because the frameworks of the systems **1** and **2** are already available,[54,55] whereas compound **3** is an extension of tricyclic azaacepentalene prepared recently by Mascal and Cerón Bertran.[69]

An important byproduct of the present investigation is that tricyclic molecules **1** and **2** are a rigid antiaromatic quasi-[12]annulene and an aromatic quasi-[14]annulene *par excellence*, respectively. They provide additional validation of Hückel's (4n + 2)π electron count rule.

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Supporting Information Available: Complete Figure 4b including all possible tautomers, Cartesian coordinates, total molecular energies, and number of imaginary frequencies. This material is available free of charge via the Internet at http://pubs.acs.org.

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