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High acidity of polycyano azatriquinanes—theoretical prediction by the DFT calculations

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Abstract—It is shown by the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) calculations that the hexacyano derivative of aza-acepentalene is an extremely powerful superacid both in the gas phase and in DMSO as evidenced by the $\Delta H_{\text{acid}} = 255.1$ kcal mol^{-1} and pK_a (DMSO) = −26.5. Its synthesis is strongly recommended, in particular, since the related conjugate base hexachloro aza-acepentalenide anion was prepared recently.

There has been a lot of interest in designing strong neutral organic acids and superacids both in the laboratory and in silico recently.[1–7] This is not surprising, because organic acids have a distinct advantage over their mineral counterparts being reactive in mild chemical environments. Moreover, superacids are vital in general acid catalysis, and their very stable anions are useful in stabilizing elusive short-lived cations like, for example, $HC_{60}{}^{+}$,[8] $C_{60}{}^{\bullet +}$,[8] C_6H^{7+},[9] etc. Several strategies have been used in tailoring superacids. The first was based on stable carborane anions and attempts to obtain the corresponding conjugate superacids.[7] The second approach utilized the concept of the electronic superacceptor substituent.[1] Our strategy was related to that of Koppel and co-workers,[1] but we used aromatization of the conjugate bases triggered by deprotonation as a prime electronic motif, enhanced by a strong anionic resonance with a number of CN substituents.[4–6] As a typical illustrative example, pentacyanocyclopentadiene[5] was synthesized last year by Richardson and Reed[10] by protonating the $C_5(CN)_5{}^{-}$ anion using electrophilic reagents derived from weakly coordinating carborane anions.

In the process of constructing new neutral organic superacids, two facets are crucial: (1) the choice of the molecular backbone and (2) the selection of appropriate substituents. Over the course of time, we have studied several hydrocarbon systems possessing a planar molecular framework and a single C(sp^3) center as a carrier of the acidic proton.[4–6] As to the substituents, it turned out that the CN group embodied the optimal compromise between strong electron-withdrawing power and very modest steric requirements. In the present letter, we report on the very high acidity of hexacyanated azatriquinanes. The choice of the systems was prompted by a recent synthesis of 10-azatriquinacene and its perchloro derivative by Mascal et al.,[11] and their monoanions, inspired by de Meijere's landmark synthesis of the triquinacene dianion.[12,13] The parent compounds studied here are depicted in Figure 1. In addition to triquinacene (**1a** and **1b**), 10-azatriquinacene **2** and its *N*-oxide derivative **3**, we also considered a precursor of the aza-acepentalenide anion—the corresponding conjugate acid **4** prepared recently by Mascal and Bertran.[14] The acidity of compounds **1a**–**4** will be discussed first. Subsequently, we shall explore acidities of their hexacyano derivatives $\mathbf{1a}_{\text{CN}}$, $\mathbf{1b}_{\text{CN}}$, $\mathbf{2}_{\text{CN}}$, $\mathbf{3}_{\text{CN}}$, and $\mathbf{4}_{\text{CN}}$ presented in Figure 2.

Acidity is calculated as the enthalpy change ΔH_{acid} for the gas-phase reaction:

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

It has two components:

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

Keywords: Acidity; Anionic resonance; Polarized continuum model; Superacids.

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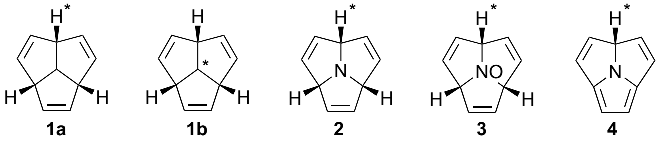

Figure 1. Schematic representation of molecules examined in the text. The site of deprotonation is denoted by an asterisk.

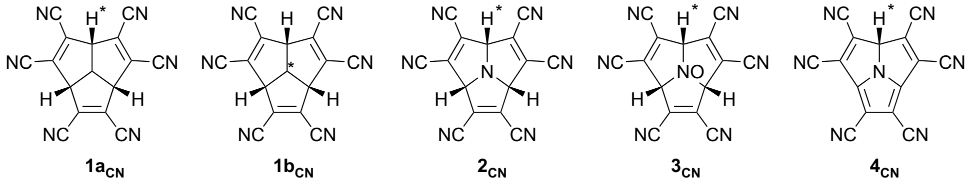

Figure 2. Schematic representation of hexacyano derivatives of examined molecules. The site of deprotonation is denoted by an asterisk.

where ΔE_{acid} denotes the change in the total molecular energy between the acid AH and its conjugate base A^-, including both the zero-point vibrational energy (ZPVE) and the finite temperature (298.15 K) correction. The second term in Eq. 2 represents the pressure–volume work contribution. It is useful to keep in mind that stronger acids have smaller numerical ΔH_{acid} values, which implies easier release of the acidic proton. The ZPVE and the temperature corrections were computed at the B3LYP/6-31G(d) level. The total molecular energies were estimated by the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) model (denoted hereafter as B3LYP). All computations were executed by using the GAUSSIAN 98 program package.[15]

The B3LYP results are presented in Table 1. It appears that deprotonation energy of the peripheral C(sp^3)–H bond in **1a** is appreciably lower than that of the central C(sp^3)–H bond (by 18.4 kcal mol^{-1}). This can be ascribed to a lower total energy of **1a**$^-$ anion (relative to **1b**$^-$ anion) in view of the anionic resonance between the lone pair and two vicinal double bonds. The deprotonation energy in **2** is practically equal to that in **1a**, but an increase in acidity is observed in **3** (by 15 kcal mol^{-1}). This is a consequence of the interaction between the lone pair and the central carbon atom, which has depleted electron density due to the strongly electronegative NO group. Finally, the highest acidity and lowest ΔH_{acid} value is found in **4** due to the anionic resonance being

Table 1. Total molecular energies of the studied molecules in the gas phase (GP) and in dimethylsulfoxide (DMSO) obtained at the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) level of theory

Molecule	E_{GP}[a]	E_{DMSO}[a]	H_{corr}[a]	ΔH_{acid}[b]	$\Delta_r H_{\text{DMSO}}$[b]	pK_a(theor)
1a	−387.06900	−387.07099	0.17763	386.7	85.0	48.5
1a$^-$	−386.43869	−386.51080	0.16116			
1b	−387.06900	−387.07099	0.17763	405.1	101.3	59.3
1b$^-$	−386.40737	−386.48295	0.15919			
$\mathbf{1a}_{\text{CN}}$	−940.65576	−940.68524	0.18017	309.3	30.3	12.3
$\mathbf{1a}_{\text{CN}}{}^-$	−940.15139	−940.21502	0.16638			
$\mathbf{1b}_{\text{CN}}$	−940.65576	−940.68524	0.18017	337.4	61.4	32.9
$\mathbf{1b}_{\text{CN}}{}^-$	−940.10381	−940.16261	0.16358			
2	−403.10432	−403.10873	0.16526	383.2	80.9	45.8
2$^-$	−402.47937	−402.55487	0.14859			
$\mathbf{2}_{\text{CN}}$	−956.68504	−956.71127	0.16777	303.9	24.2	8.3
$\mathbf{2}_{\text{CN}}{}^-$	−956.18925	−956.25073	0.15397			
3	−478.28050	−478.29559	0.16991	372.0	71.2	39.4
3$^-$	−477.67442	−477.75836	0.15437			
$\mathbf{3}_{\text{CN}}$	−1031.84506	−1031.87259	0.17177	297.9	18.1	4.3
$\mathbf{3}_{\text{CN}}{}^-$	−1031.35946	−1031.42238	0.15859			
4	−401.93958	−401.94343	0.14225	335.6	27.8	10.7
4$^-$	−401.39307	−401.47691	0.12819			
$\mathbf{4}_{\text{CN}}$	−955.51158	−955.54103	0.14426	255.1	−28.5	−26.5
$\mathbf{4}_{\text{CN}}{}^-$	−955.09555	−955.16646	0.13247			

H_{corr} denotes thermal correction to enthalpy obtained by the B3LYP/6-31G(d) model. Theoretical pK_a values are obtained using Eq. 4.

[a] In atomic units.

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

completely spread over the whole molecular perimeter. The resulting ΔH_{acid} value equals 335.6 kcal mol^{-1}.

Hexacyanation exerts a dramatic effect on the investigated compounds (Table 1). The increase in acidity upon cyanation is given within parentheses (in kcal mol^{-1}): $\mathbf{1a}_{\text{CN}}$ (77.4), $\mathbf{1b}_{\text{CN}}$ (67.7), $\mathbf{2}_{\text{CN}}$ (79.3), $\mathbf{3}_{\text{CN}}$ (74.1), and $\mathbf{4}_{\text{CN}}$ (80.5). The largest amplification is found in $\mathbf{4}_{\text{CN}}$, which represents a very strong superacid assuming a ΔH_{acid} value as low as 255.1 kcal mol^{-1}. The origin of highly acidic and superacidic ΔH_{acid} values of hexacyanated derivatives can be traced down to the anionic resonance, which is considerably enhanced by a concerted resonance effect of six CN groups.

Our next task was to estimate acidities in DMSO, which has a number of favorable features as a solvent.[16,17] Hence, we considered the proton transfer reaction (3) between acids in question and solvent molecules taking place in solution:

$$\text{AH} + \text{DMSO} \rightarrow \text{A}^- + \text{DMSOH}^+ + \Delta_r H_{\text{DMSO}} \tag{3}$$

by employing the isodensity polarized continuum model (IPCM)[18,19] at the DFT level described earlier.[6] The enthalpies of proton transfer $\Delta_r H_{\text{DMSO}}$ are very well correlated with the experimental pK_a values for a wide variety of neutral organic acids[6] resulting in a semiempirical correlation:

$$\text{p}K_a(\text{theor}) = 0.661 \cdot \Delta_r H_{\text{DMSO}} - 7.7 \tag{4}$$

with the average absolute error of 1.1 (in pK_a units) and $R^2 = 0.985$. Hence, the predicted acidities in DMSO should be quite reliable.

Perusal of the results presented in Table 1 shows that the parent compounds **1a**–**4** are weak acids in DMSO, with the system **4** being a notable exception. It exhibits a moderate acidity with pK_a (**4**) = 10.7. However, cyanation leads to enhancement of acidity achieving a record superacidic value pK_a = −26.5 kcal mol^{-1} in $\mathbf{4}_{\text{CN}}$.

In conclusion, we would like to strongly recommend a synthesis of hexacyano derivative $\mathbf{4}_{\text{CN}}$. It should be noted that the hexachloro derivative of $\mathbf{4}^-$ anion has been prepared[14] and that the procedure of replacing chlorine atoms by the CN group is known.[20] The final step includes protonation of the $\mathbf{4}_{\text{CN}}{}^-$ anion.

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