Extremal acidity of Rees polycyanated hydrocarbons in the gas phase and DMSO – a density functional study

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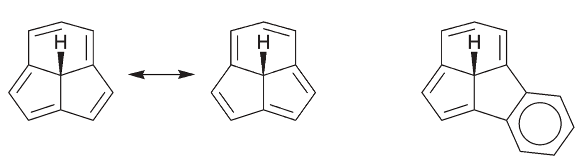
It is shown by using the density functional theory (DFT) calculations that Rees tricyclic[10]annulene 1 and its benzo-annelated derivative 2, substituted by CN groups at all peripheral sp^2 carbon positions, represent hyperstrong neutral superacids in the gas-phase and DMSO.

In the nineteen-eighties Rees and coworkers[1–6] synthesized tricyclic[10]annulene **1** and its benzo-fused derivative **2** (Fig. 1), as well as a number of compounds obtained by various substituents. Unlike floppy monocyclic [10]annulene, which is highly distorted and nonplanar and thus devoid of aromatic character,[7,8] Rees and coworkers have shown that 7b*H*-cyclopent[*cd*]indene structure **1** exhibited typical aromatic features[1–5] as indicated by the resonance structures in Fig. 1. The reason is that the central tetrahedral C(sp^3) carbon atom brings rigidity into the system, thus enabling a good overlapping between the atomic 2p orbitals along the π-electron perimeter despite some nonplanarity. The same holds for the related benzo-annelated compound **2**. It is the aim of the present work to examine acidity of systems **1** and **2** in the gas-phase and dimethyl sulfoxide (DMSO) and to show that their polycyano derivatives **3** and **4** (Fig. 2) are hyperstrong neutral organic acids. In doing so we use modern computational chemistry models and methods, which in turn provide useful information complementary to the experimental data.[9] Our method of choice is the density functional theory (DFT) B3LYP/6-311 + G(2d,p)//B3LYP/6-31G(d) scheme (abbreviated as B3LYP). A flexible 6-311 + G(2d,p) basis set is used in the single point calculations, since the triple-zeta sets give the total molecular energies, estimated at this level of theory, very close to their asymptotic values.[10] This selection of the method, that represents a good compromise between accuracy and practicality, is corroborated by its success in reproducing molecular electron affinities[11–13] and acidities.[14–16]

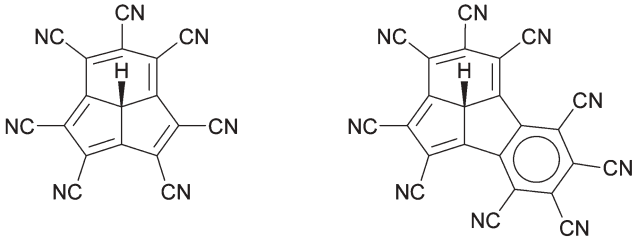
As a measure of acidity we use the enthalpy change $\Delta H_{\rm acid}$ for the gas-phase reaction:

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



1 2

Fig. 1 Schematic representation of two most important resonance structures of tricyclic[10]annulene **1** and its benzo-annelated derivative **2**.



3 4

Fig. 2 Schematic representation of seven- and nine-fold cyanated derivatives of **1** and **2**, respectively.

where $\Delta H_{\rm acid} = \Delta E_{\rm acid} + \Delta(pV)$. Here, $\Delta E_{\rm acid}$ is the change in the total energy of 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 term $\Delta(pV)$ denotes the pressure–volume work contribution. The ZPVEs and the temperature corrections are computed at the B3LYP/6-31G(d) level. All calculations are performed by using the GAUSSIAN 98 program.[17]

The calculated $\Delta H_{\rm acid}$ values for **1** and **2** are 331.1 and 318.0 kcal mol^{-1}, respectively, implying that they are moderately strong acids. It is interesting to compare their acidities with those of some known mineral acids. For instance, tricyclic[10]annulene **1** is close in its acid strength to H_3PO_4 and HCl, which have the $\Delta H_{\rm acid}$ values of 330.5 and 333.4 kcal mol^{-1}, respectively.[18] Similarly, $\Delta H_{\rm acid}(\mathbf{2})$ = 318.0 kcal mol^{-1} compares to $\Delta H_{\rm acid}$(HI) = 314.3 and $\Delta H_{\rm acid}$(CF_3COOH) = 322.8 (in kcal mol^{-1}).[18] The most acidic proton in both cases belongs to the central C(sp^3)–H bond. The resulting anions are planar in order to ensure the optimal resonance effect. This is interesting, because both conjugate bases $\mathbf{1}^{-}$ and $\mathbf{2}^{-}$ possess antiaromatic number of π-electrons 12 and 16, respectively. In order to shed some more light on this puzzling feature, let us analyse the parent compound **1** in some more detail. The variation in the perimeter C–C bond distances spans a very close range between 1.395–1.423 Å (Scheme 1), which in turn is usually found in aromatic molecules. Thus, it is justified to characterize **1** as a quasi-[10]annulene system. This conjecture is in accordance with its electrophilic reactivity,[3,4] photoelectron spectra[19] and diatropicity reflected in the NMR H-chemical shifts $\delta_{\rm H}$.[2] The corresponding anion $\mathbf{1}^{-}$ is planar with C–C bond distances displayed in Scheme 1. Their range is enlarged (1.390–1.464 Å), but they still reflect a pronounced π-electron delocalization. The latter can be visualized by the Pauling's resonance structures depicted in Scheme 2. It should be noticed that in two resonance structures the aromatic stabilization of the

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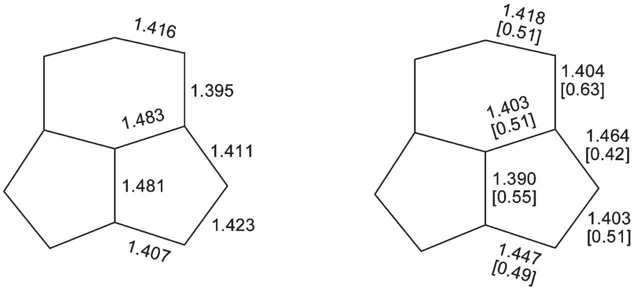
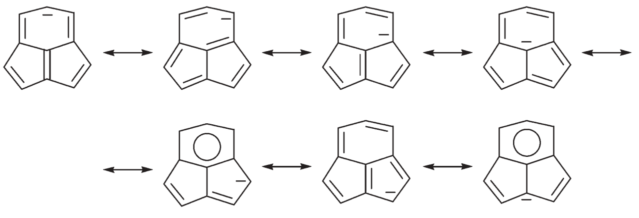


1 **1**$^-$

Scheme 1 Schematic representation of tricyclic [10]annulene **1** and its anion **1**$^-$. Characteristic bond lengths (in Å) are computed by the B3LYP/6-31G(d) model. Löwdin π-bond orders in the planar anions are given within the squared parentheses.



Scheme 2 The resonance structures of anion **1**$^-$.

benzene ring is almost fully preserved. This is also evident by considering the corresponding C–C bond distances (Scheme 1). The π-electron bond orders obtained by Löwdin's symmetric partitioning[20] of the mixed density are placed between 0.4–0.6 |e|, which is close to that in benzene. Finally, Schleyer's NICS(1)[21] and $\text{NICS}(1)_{zz}$[22] nuclear independent chemical shifts indicate that all three rings in **1**$^-$ are stabilized, where $\text{NICS}(1)_{zz}$ denotes the z-component of the magnetic shielding tensor. They are given in the form of diads: [NICS(1); $\text{NICS}(1)_{zz}$], which for the six- and five-membered rings in **1**$^-$ read: [−14.5; −36.2] and [−6.7; −13.7] in ppm, respectively. The reference values in benzene [−12.8; −32.2] and cyclopentadienyl anion [−14.0; −36.2] show that the six-membered ring fragment in **1**$^-$ is aromatic, whereas the five-membered rings in **1**$^-$ are stabilized by the anionic resonance, but to a considerably lesser extent than in a free cyclopentadienyl anion. It follows as a corollary that planar polycyclic anions can be quite stable despite a formal antiaromatic number of the π-electrons, since the individual rings are either fully of partially aromatic. A similar conclusion holds for the anion **2**$^-$. The increase in acidity upon seven- and nine-fold cyanation in **3** and **4** is dramatic indeed, since the corresponding values are as low as 247.0 and 237.1 kcal mol^{-1}, respectively. It is noteworthy that the conjugate bases **3**$^-$ and **4**$^-$ are planar too exhibiting even stronger anionic resonance, as evidenced by a considerably larger number of the resonance structures. It is of interest to put these results into perspective by comparison with some known very strong Brønsted mineral 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.[18] Starting from eqn. (2) relating Gibbs free energy with the thermodynamic reaction constant K_{acid} for deprotonation:

$$\Delta G_{\text{acid}} = -R\cdot T\cdot \ln(K_{\text{acid}}) \qquad (2)$$

one can approximately estimate a difference in acidity between molecules **3** and **4** and $HClO_4$. It is easy to show that $\Delta\log(K_{\text{acid}}) \cong \Delta\Delta H_{\text{acid}}/1.36$, if the contribution of the $\Delta(T\Delta S)$ entropy term can be neglected. Tacitly assuming that the latter is justified, it follows that, compared to $HClO_4$, molecules **3** and **4** are around 30 and 37 orders of magnitude stronger acids in the gas-phase. Consequently, the cyano groups exert enormous acidifying effect as has been found in other organic compounds recently.[23–26] The origin of the highly pronounced acidity was identified to be aromatization of the central carbon moiety and a strong anionic resonance effect with numerous CN groups as *e.g.* in pentacyanocyclopentadiene[25] and nonacyanocyclononatetraene.[27] The systems **1–4** studied here are distinctly different being formally antiaromatic upon the proton detachment and yet **3** and **4** are hyperstrong acids. Obviously, the anionic resonance effect assisted by a number of CN groups is a decisive factor.

A point of outmost importance is the behaviour of strong superacids in solvents of moderate polarity. One of the most suitable solvents is DMSO due to its large dielectric constant and pronounced dissociative power.[28,29] A quite accurate method in treating the solvent effects is given by the use of the complete basis set CBS-QB3 approach based on the polarizable conductor method, which gives good agreement with experiment as evidenced by the root-mean-square error less than 0.4 pK_a units for smaller molecules.[30,31] Unfortunately, this approach is not feasible in large systems. Hence, we shall examine acidity of compounds **1–4** in DMSO by using the isodensity polarized continuum model (IPCM)[32,33] in conjuction with the B3LYP/6-311 + G(2d,p)//B3LYP/6-31G(d) method. We employ the proton transfer reaction (3) between solute and the DMSO solvent molecule taking place in solution:

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

The enthalpies of the proton transfer reactions $\Delta_r H_{\text{DMSO}}$ were correlated with the experimental pK_a values for a wide variety of CH acids yielding a very good linear correlation:[27]

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

with an average absolute error of 1 pK_a unit and the correlativity factor $R^2 = 0.985$. This accuracy is sufficient for our purpose.

The estimated pK_a values by eqn. (4) for **1**, **2**, **3** and **4** are 7.9, −0.5, −20.5 and −30.4, respectively. It appears that pure hydrocarbon **2** is already appreciably acidic. A dramatic amplification is obtained for the polycyano derivative **3**, which is very strongly acidic being comparable to pentacyanocyclopentadiene (pK_a = −20.2) and substantially surpassing *e.g.* nonacyanocyclononatetraene (pK_a = −14.8).[27] An absolute record holder is molecule **4** with pK_a = −30.4. It is an acid of unprecedented strength.

It was shown that strong superacids proved useful in producing new reactive cations derived from weak bases, like *e.g.* HC_{60}^+ and $C_{60}^{\bullet+}$,[34] $C_6H_7^+$,[35] Bu_3Sn^{+}[36] and $Cu(CO)_4^+$.[37] One concludes, by extending the argument, that polycyanated Rees hydrocarbons, once synthesized, will considerably extend the list of new stabilized cations. In addition, by forming highly stable anions these ultrastrong acids will provide negatively charged species of potential interest in designing novel materials.[38] It is also useful to recall that neutral organic (super)acids have some distinct advantages over their inorganic counterparts. In particular, the negative charge in large organic conjugate bases is dispersed over many centers unlike in small mineral acids. This favourable feature decreases aggregation of solutes and increases solubility in common organic solvents.[28] Moreover, such property leads to a lower nucleophilicity and low basicity of the produced anions, which might lead to a nonoxidativity, pronounced inertness and a weak coordinating ability of the produced anions.[38] Hence, the efforts to synthesize compounds **3** and **4** is strongly recommended.

It is conceivable that it will be easier to prepare very stable anions rather than the corresponding superacids. However, a recent pioneering success of Richardson and Reed in protonating pentacyanocyclopentadienyl anion[39] shows that the synthesis of very strong superacids is also feasible. For this purpose it is gratifying that the extensive knowledge necessary for preparation of polycyanated planar hydrocarbons is available.[40–42]

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