The Acidity of Brønsted CH Acids in DMSO − The Extreme Acidity of Nonacyanocyclononatetraene

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The gas-phase (GP) acidity of a large variety of CH organic acids is studied by a carefully selected B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) theoretical model. Acidities are mirrored by the proton affinities of the corresponding conjugate bases. A very good agreement with available experimental data is achieved. It is concluded that the model applied has a high predictive value and that theoretical $PA(\text{anion})_{GP}$ values can be used instead of measured data in cases where experiments are not feasible or not performed. It is shown, employing the isodensity polarized continuum model (IPCM), that there is a good linear relationship between the enthalpies of the proton-transfer reactions in DMSO and the observed pK_a(DMSO) values. This relation can be used in predicting the acidity of strong, neutral organic superacids. As an illustrative case, the acidity of cyclononatetraene-1,2,3,4,5,6,7,8,9-nonacarbonitrile ("nonacyanocyclononatetraene") is considered. It is conclusively shown that this compound should be a very potent superacid, as evidenced by its $PA(\text{anion})_{GP}$ (260.0 kcal·mol^{-1}) and pK_a (–14.8). The origin of high acidity is identified as a very strong anionic resonance effect in the resulting conjugate base.

Introduction

Proton transfer is a ubiquitous reaction that is of paramount importance in chemistry and biochemistry. It is intimately related to the notions of acidity and basicity, which are important pillars of these two chemical disciplines that provide a bridge between modern physics and molecular biology. Brønsted acidity is a measure of the propensity of a molecule to donate a proton and to accommodate the negative charge in the resulting anions, whereas Brønsted basicity is the ability to accept a proton and to distribute the positive charge over the base as efficiently as possible. It is common knowledge that both acids and bases contributed immensely to the understanding of the (electronic) structure−reactivity relationship in the middle of the last century, thus providing the cornerstone for the development of physical organic chemistry. In addition, organic acids serve as catalysts in a variety of chemical and biochemical reactions, thus playing a crucial role not only in physical organic and synthetic chemistry as well as in the processes of life, but also in chemical engineering and industrial applications. It is well-known that neutral organic acids have advantageous features, one of which is that the anions produced under mild reaction conditions participate in a number of useful chemical transformations. For example, weakly coordinating anions are important in olefin polymerisation[1] and provide promising ingredients in new lithium-based battery technology.[2] Moreover, reactions between acids and bases in the gas phase can be directly related to intrinsic reactivity free of solvent effects.[3−5] However, the majority of chemical reactions take place in solution, thus making the understanding and prediction of the solvent influence an important issue. We shall focus in the present work on the acidity of C−H bonds in organic compounds, which is the key feature of a very rich carbanion chemistry.[6] It is not surprising, therefore, that CH acids have been subjected to numerous experimental[7−12] and theoretical studies[13−15] in the last decades. It should be pointed out in this respect that computational chemistry is an important complement to experimental examinations nowadays, since it can treat systems that are not amenable to measurements to a good accuracy.[16,17] In addition, theory can offer a simple and intuitively appealing interpretation of the acidity features.[18,19]

Recently, a strong emphasis has been placed on the design of very potent neutral organic superacids in silico.[20−23] The largest body of theoretical results, however, refers to the gas phase; estimates of acidity in solutions are scarce. Since solvent effects can have a dramatic influence on the rates and thermodynamic equilibria in chemical reactions, more investigations in this direction are highly desirable. It is the aim of the present work to establish a relationship between empirical pK_a values in DMSO and

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theoretical enthalpies of deprotonation for a large variety of CH acids. Subsequently, this linear relationship will be applied in predicting the acidity of some new superacids in this important solvent.

Theoretical Procedure

Acidity is given by the enthalpy change, ΔH_{acid}, for the gas-phase reaction

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

and is calculated as

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

where ΔE_{acid} is the change in the total energy of the participating species in reaction (1). It includes both the zero-point vibrational energy (ZPVE) and the finite temperature (298.15 K) correction. The pressure−volume work term is denoted 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 the G3 computational scheme[24] is very successful in predicting acidities and basicities in the gas phase. However, computations to be performed on a large number of sizeable molecules require a feasible and more practical model. For this purpose we selected the DFT-B3LYP method,[25,26] which offers the best compromise between accuracy and computational efforts, provided an appropriate basis set is chosen. It has been shown by Handy and co-workers[27] that Pople's triple-zeta basis set, which includes the polarization and diffuse functions, yields practically converged energies at the B3LYP level. Hence, our basis sets of choice were B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d), implying that geometries were optimised by the very economical 6-31G(d) functions, whereas the energetics were treated by a very flexible 6-311+G(2d,p) basis set necessary for a satisfactory description of the anionic species. It is noteworthy that the DFT-B3LYP approach has proved very useful in reproducing electron affinities.[28−30] Finally, the ZPVE and thermal corrections were estimated by the B3LYP/6-31G(d) method.

Modern computational chemistry can do a decent job in describing isolated molecules in the gas phase. More specifically, there is a general consensus of opinion that theory can predict the acidity and basicity of small molecules in the gas phase as well as, or even better than, experiment.[31] However, the situation is different and less satisfactory in solution. It is gratifying, however, that a simple dielectric continuum model properly accounts for long-range bulk-solvent effects for moderately polar solvents[31−33] in a reasonably accurate way. The influence of the DMSO solvent is considered by using the isodensity polarized continuum model (IPCM) developed by Miertuš and Tomasi[32,33] with a definition of the cavity proposed by Wiberg and co-workers.[34,35] Our calculations are based on the proton-transfer reaction (3) between solute AH and the DMSO, which ultimately leads to the formation of A^{-} in the solution

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

where AH denotes the acid in question. The total molecular enthalpies in the solution of all species entering Equation (3) are denoted as $\Delta_r H_{DMSO}$ and are obtained by the IPCM/B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) model, which includes the thermal correction to enthalpy obtained at the B3LYP/6-31G(d) level. No scaling factor was used for the obtained frequencies necessary to calculate the thermodynamic parameters.

All calculations were performed with the GAUSSIAN 98 suite of programs.[36]

Results and Discussion

The neutral organic CH acids explored in this paper can be divided into four groups: nitriles (**1a−1d**), benzylnitriles (**2a−2k**), and malononitriles (**3a−3i**), depicted in Figure 1, and a family of hydrocarbons possessing a CH_3 or CH_2 group attached to, or forming part of, planar aromatic and nonaromatic structures, respectively, as shown in Figure 2. The results are summarized in Table 1 for the nitrile-containing compounds and Tables 2 and 3 for the rest.

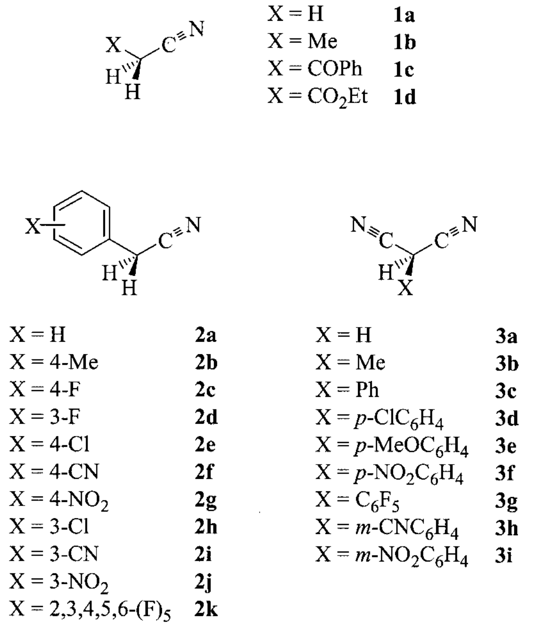


Figure 1. Schematic representation of the nitriles, benzylnitriles and malononitriles studied here

Let us commence discussion with the gas-phase (GP) proton affinities of the conjugate bases. Theoretical PA_{GP} values can be favourably compared with the experimental data compiled by NIST.[37] The best index of the overall compatibility is given by the average absolute error, Δ_{abs}. If we take into account the reported PA_{exp} values, then Δ_{abs} is

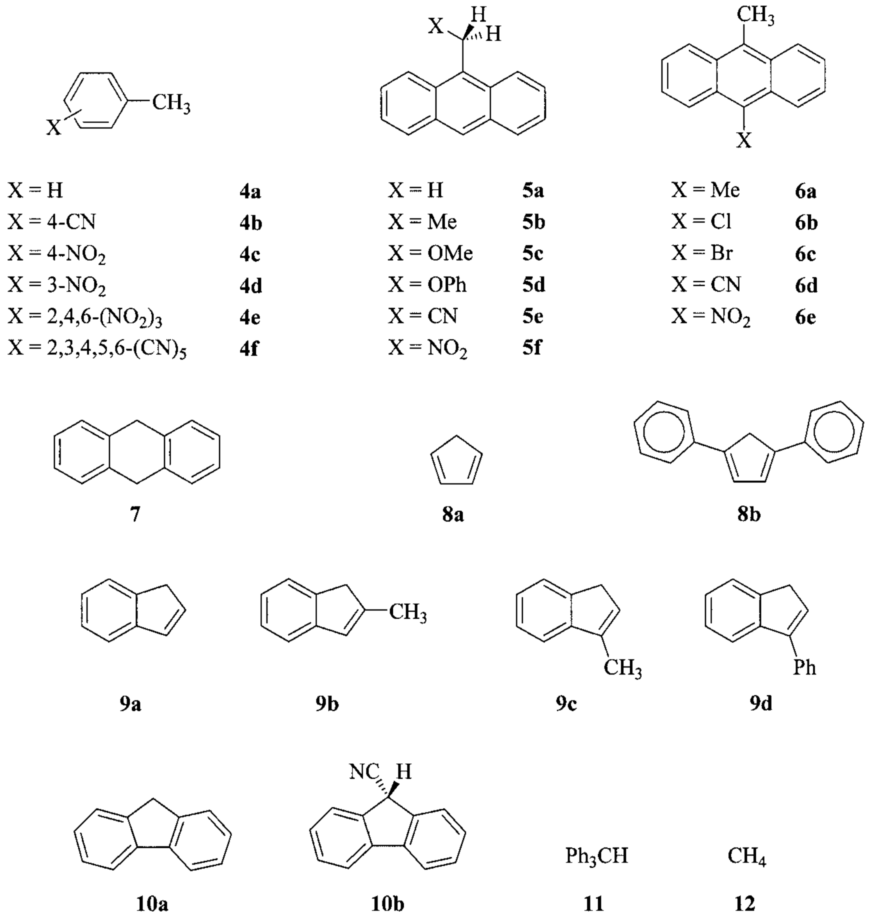


Figure 2. Schematic representation of the CH acids possessing planar aromatic or nonaromatic backbones studied here

3.2 kcal·mol^{-1}. However, if the experimental error margin is taken in a way that the measured value is as close to the theoretical result as possible, then $\Delta_{abs} = 1.7$ kcal·mol^{-1}. It follows that the adopted B3LYP model is quite reliable and that it has a predictive ability, which is a prerequisite in investigating new acids and superacids. In other words, theoretical results can serve as a good first approximation to the true values of acidity in molecules for which the experimental data are not available (Table 1). According to our calculations the most acidic compound is **3f**, with a PA_{GP} close to 300 kcal·mol^{-1}, followed by **3i**, with a PA_{GP} of 304 kcal·mol^{-1}. In both cases malononitrile is substituted by a benzyl fragment with a nitro group attached at the *para* and *meta* positions, respectively. It is fair to say that **3f** and **3i** exhibit superacidic properties in the gas phase. The least acidic compound known is CH_4, therefore it is astounding that methane substituted by three electron-acceptor groups becomes a powerful superacid.

We shall focus now on the acidity of the studied molecules in a non-protic solvent, DMSO, which is known to possess a low polarity. The enthalpies of the proton-transfer reaction in DMSO (3) are given in Table 1 under the heading $\Delta_r H_{DMSO}$. This is the point of departure from theory to experiment — namely, in estimating pK_a values theory heavily leans on the experimental measurements. The best one can achieve is to find a relation between $\Delta_r H_{DMSO}$ and pK_a(exp) in the least-squares sense. One obtains:

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

which is a straight line over a wide range of pK_a values between −1.8 (**3f**) and 56.0 (**12**). The scatter of the points is moderate (Figure 3) and the statistical parameters reveal a high correlativity of the calculated $\Delta_r H_{DMSO}$ data and the experimental pK_a values ($R^2 = 0.985$).

The average absolute deviation from experiment is $\Delta_{abs}(pK_a) = 1.1$. This is close to the experimental error and, consequently, it is fair to say that the empirical relation (4) provides a satisfactory description of the acidity in DMSO and has predictive value at the same time. It is interesting to note that solvent effects in DMSO do not change much the hierarchy in acidity that exists already in the gas phase — **3f**, **3g** and **3i** remain the most acidic compounds. The difference is that **3g** is somewhat more acidic in DMSO than **3i**. A closer look reveals that the trend in the gas phase and DMSO is the same.

Our B3LYP theoretical model of choice and formula (4) were used to predict the gas-phase and solution (DMSO) acidity of cyclononatetraene (**13**) and its nonacyano derivative **14a** (Figure 4).

Table 1. Energetic properties of CH acids **1a**−**1e**, **2a**−**2k**, and **3a**−**3i** obtained by the selected B3LYP approach described in the text (in au); a comparison between the proton affinities of the corresponding conjugate bases in the gas phase PA_{GP} and the measured data is given in kcal·mol^{-1}; theoretical pK_a(thr) values are obtained from Equation (4)

Molecule	E_{GP}	E_{solv}	H_{corr}	PA_{GP}	PA_{exp}	Δ_rH_{DMSO}	pK_a(thr)	pK_a(exp)	Δ(pK_a)
1a	−132.79881	−132.80942	0.05018			58.3	30.8	31.3	0.5
1a$^-$	−132.19387	−132.29339	0.03529	371.7	372.9 ± 2.1				
1b	−172.12403	−172.13455	0.08043			61.0	32.7	32.5	0.2
1b$^-$	−171.51492	−171.61355	0.06493	374.0	375.0 ± 2.1				
1c	−477.26999	−477.28854	0.14786			26.7	9.9	10.2	0.3
1c$^-$	−476.73049	−476.82425	0.13427	331.5	326.3 ± 2.0				
1d	−400.06892	−400.08574	0.12770			31.5	13.1	13.1	0.0
1d$^-$	−399.51997	−399.61333	0.11379	337.2	339.9 ± 2.3				
2a	−363.90805	−363.91876	0.13616			41.4	19.7	21.9	2.2
2a$^-$	−363.34368	−363.42993	0.12153	346.4	350.7 ± 2.3				
2b	−403.23689	−403.24881	0.16556			45.0	22.0	22.9	0.9
2b$^-$	−402.66985	−402.75425	0.15092	348.1	351.6 ± 2.5				
2c	−463.17855	−463.19117	0.12875			43.9	21.3	22.2	0.9
2c$^-$	−462.61695	−462.69862	0.11432	344.8	349.0 ± 2.1				
2d	−463.17884	−463.18994	0.12875			40.8	19.3	20.0	0.7
2d$^-$	−462.62280	−462.70221	0.11430	341.3	–				
2e	−823.53238	−823.54264	0.12770			42.5	20.4	20.5	0.1
2e$^-$	−822.97699	−823.05244	0.11347	341.1	345.1 ± 2.3				
2f	−456.17511	−456.19368	0.13649			36.8	16.6	16.0	0.6
2f$^-$	−455.63958	−455.71298	0.12265	328.8	334.5 ± 2.3				
2g	−568.47610	−568.49526	0.14126			29.7	11.9	12.3	0.4
2g$^-$	−567.95144	−568.02608	0.12758	322.1	329.3 ± 2.3				
2h	−823.53243	−823.54504	0.12770			40.5	19.0	19.5	0.5
2h$^-$	−822.97880	−823.05792	0.11330	339.8	344.5 ± 2.3				
2i	−456.17484	−456.19315	0.13650			39.0	18.1	18.7	0.6
2i$^-$	−455.63067	−455.70841	0.12221	334.0	–				
2j	−568.47599	−568.49553	0.14129			38.2	17.5	18.1	0.6
2j$^-$	−567.93335	−568.01218	0.12703	333.0	337.5 ± 2.5				
2k	−860.22517	−860.23756	0.09976			35.2	15.6	15.8	0.2
2k$^-$	−859.68405	−859.75884	0.08543	332.0	–				
3a	−225.04741	−225.06402	0.05066			26.7	9.9	11.0	1.1
3a$^-$	−224.51061	−224.59985	0.03721	329.9	335.8 ± 2.1				
3b	−264.37475	−264.38970	0.08053			28.2	10.9	12.4	1.5
3b$^-$	−263.83284	−263.92310	0.06702	333.1	–				
3c	−456.15658	−456.17183	0.13630			15.6	2.6	4.2	1.6
3c$^-$	−455.64371	−455.72557	0.12313	315.0	321.6 ± 2.1				
3d	−915.77992	−915.79573	0.12780			14.6	1.9	3.1	1.2
3d$^-$	−915.27498	−915.35139	0.11489	310.2	–				
3e	−952.46810	−570.72994	0.17166			18.1	4.3	5.7	1.4
3e$^-$	−951.96786	−570.27959	0.15845	307.1	–				
3f	−660.72153	−660.74314	0.14131			6.1	−3.7	−1.8	1.9
3f$^-$	−660.23926	−660.31247	0.12863	296.1	305.2 ± 2.3				
3g	−952.46810	−952.48666	0.09974			12.9	0.8	0.3	0.5
3g$^-$	−951.96786	−952.04444	0.08634	307.0	303.6 ±2.0				
3h	−548.42088	−548.44593	0.13659			15.8	2.8	2.2	0.6
3h$^-$	−547.92508	−547.99947	0.12359	304.4	–				
3i	−660.72181	−660.74724	0.14137			15.2	2.3	1.7	0.6
3i$^-$	−660.22674	−660.30183	0.12836	304.0	–				

The corresponding values are presented in Table 3. It is important to realize that the latter compound possesses two prototropic tautomers: the C(sp^3)−H-bonded molecule **14a** and system **14b** involving a C=NH *exo* fragment. Our calculations reveal that they are both of comparable stability, with **14b** being less stable by 0.5 kcal·mol^{-1} and 1.4 kcal·mol^{-1} at the B3LYP/6-31G(d) and B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) levels of theory, respectively. Accordingly, we shall only consider systems **13** and **14a**. These compounds should be acidic, since a pattern of 10 aromatic π-electrons should be formed upon deprotonation. This intuitive conclusion is corroborated by an inspection of the data given in Table 3. The gas-phase acidity of **13**, mirrored through the proton affinity of the corresponding conjugate base, has a value of 335.7 kcal·mol^{-1}, which shows that this hydrocarbon is rather acidic. However, a dramatic enhancement of its acidity can be accomplished by multiple cyanation of the starting molecule **13**. The highest value is achieved in its nonacyano derivative **14a**, where the gas-phase proton affinity of the anion **14a**$^-$ is 260.0 kcal·mol^{-1}. This remarkable acidity indicates that nonacyanocyclononatetraene (**14**) is a superacid of unprecedented

Table 2. Energetic properties of the CH acids **4a**−**4f**, **5a**−**5f**, and **6a**−**6e** obtained by the selected B3LYP approach described in the text (in au); a comparison between the proton affinities of the corresponding conjugate bases in the gas phase PA_{GP} and the measured data is given in kcal·mol^{-1}; theoretical pK_a(thr) values are obtained from Equation (4)

Molecule	E_{GP}	E_{solv}	H_{corr}	PA_{GP}	PA_{exp}	Δ_rH_{DMSO}	pK_a(thr)	pK_a(exp)	Δ(pK_a)
4a	−271.64587	−271.64877	0.13547			71.0	39.2	43.0	3.8
4a$^-$	−271.02477	−271.11108	0.11911	381.0	380.6 ± 1.0				
4b	−363.91552	−363.92637	0.13589			56.6	29.7	30.7	1.0
4b$^-$	−363.33165	−363.41305	0.12097	358.5	360.5 ± 2.4				
4c	−476.21701	−476.22698	0.14069			41.6	19.8	20.4	0.6
4c$^-$	−475.64971	−475.73792	0.12611	348.3	352.5 ± 2.1				
4d	−476.21634	−476.22636	0.14071			63.4	34.2	33.5	0.7
4d$^-$	−475.62079	−475.70122	0.12490	365.3	362.9 ± 2.1				
4e	−885.32904	−885.35880	0.15052			31.0	12.8	10.4	2.4
4e$^-$	−884.81438	−884.88778	0.13713	316.0	315.6 ± 2.2				
4f	−732.94335	−732.97860	0.13601			28.6	11.2	8.2	3.0
4f$^-$	−732.44177	−732.51165	0.12284	308.0	−				
5a	−578.99777	−579.01100	0.23468			58.9	31.3	31.1	0.2
5a$^-$	−578.40986	−578.49290	0.21870	360.4	362.2 ± 2.4				
5b	−618.32191	−618.33386	0.26502			63.6	34.3	32.4	1.9
5b$^-$	−617.73043	−617.80800	0.24866	362.4	−				
5c	−693.54680	−693.55888	0.27055			59.5	31.6	30.6	1.0
5c$^-$	−692.96057	−693.03967	0.25444	359.2	−				
5d	−885.34254	−885.35611	0.32646			57.9	30.6	30.2	0.4
5d$^-$	−884.76062	−884.83922	0.31002	356.3	−				
5e	−671.25953	−671.27603	0.23546			43.2	20.8	19.7	1.1
5e$^-$	−670.70738	−670.78413	0.22059	338.6	−				
5f	−783.56310	−783.58121	0.24080			31.4	13.1	12.7	0.4
5f$^-$	−783.01316	−783.10786	0.22575	337.1	−				
6a	−618.31903	−618.33221	0.26469			62.3	33.5	31.8	1.7
6a$^-$	−617.73161	−617.80851	0.24856	360.0	−				
6b	−1038.61918	−1038.63189	0.22654			57.0	30.0	28.2	1.8
6b$^-$	−1038.04151	−1038.11735	0.21113	354.3	−				
6c	−3152.53168	−3152.54351	0.22656			57.1	30.0	28.4	1.6
6c$^-$	−3151.95601	−3152.02885	0.21108	353.0	−				
6d	−671.26720	−671.28471	0.23527			46.2	22.8	20.0	2.8
6d$^-$	−670.71030	−670.78808	0.22047	341.6	−				
6e	−783.55593	−783.57506	0.24003			35.2	15.6	13.2	2.4
6e$^-$	−783.01114	−783.09597	0.22529	334.1	−				

strength whose synthesis is highly desirable. It is noteworthy that cyclononatetraene anion **13**$^-$ has been prepared as its potassium or tetramethylammonium salt.[38,39] The high acidity of **13** and **14a** is maintained in DMSO solution as well. The calculated enthalpies of proton transfer (3) from the acid in question to the DMSO molecule in solution are Δ_rH_{DMSO} = 27.7 kcal·mol^{-1} and −10.7 kcal·mol^{-1} for molecules **13** and **14a**, respectively. The latter value, being negative, strongly suggests that the proton transfer from **14a** is highly pronounced and that this process strongly favours the formation of **14a**$^-$. In other words, this value strengthens our conclusion that **14a** is a very potent superacid. Taking into account these numbers and applying Equation (4), we obtain theoretical acidity constants, pK_a(thr), in DMSO for the highly acidic compounds **13** and **14a** as low as 10.6 and −14.8, respectively (thr within parentheses denotes that this is a theoretical estimate). It is hoped that the present predictions will be of some value in experimental research.

The gas-phase structural parameters offer an interesting insight into the properties of these strong acids. Some characteristic bond lengths calculated at the B3LYP/6-31G(d) level of theory are given in Figure 5.

The parent cyclononatetraene **13** is non-planar (Scheme 1) and exhibits expected bond lengths for localized single and double bonds.

Deprotonation at C(sp^3) centre yields the conjugate base **13**$^-$ and triggers a strong anionic resonance effect, which is amplified by the complete planarization of the molecular skeleton and formation of the perfectly symmetrical D_{9h} structure. This is in full accordance with the previous results of Boche and co-workers,[40,41] who reported a planar D_{9h} structure of the cyclononatetraenyl anion **13**$^-$ as revealed by an NMR experiment. It is interesting to mention that all C−C bond lengths in **13**$^-$ assume a value of 1.404 Å and a Löwdin π-bond order of 0.63, both of which are close to the values found in benzene (1.398 Å and 0.66). Therefore, one concludes that the **13**$^-$ anion is an aromatic species. Ninefold substitution by the strong electron-acceptor group CN in **14a** introduces some changes in the geometrical parameters, but the general conclusions remain the same. In neutral molecule **14a** all carbon−carbon bonds are notably longer than those in the parent system **13**. Proton loss at an sp^3 carbon centre shortens C−C single bonds and elongates C=C double bonds over the molecular perimeter, but to a smaller extent than in the **13**/**13**$^-$ parent com-

Table 3. Energetic properties of the CH acids **7**, **8a**, **8b** **9a−9d**, **10a**, **10b**, **11−13**, and **14a** obtained by the selected B3LYP approach described in the text (in au); a comparison between the proton affinities of the corresponding conjugate bases in the gas phase PA_{GP} and the measured data is given in kcal·mol^{-1}; theoretical pK_a(thr) values are obtained from Equation (4)

Molecule	E_{GP}	E_{solv}	H_{corr}	PA_{GP}	PA_{exp}	Δ_rH_{DMSO}	pK_a(thr)	pK_a(exp)	Δ(pK_a)
7	−540.88250	−540.88784	0.22853			53.8	27.8	30.1	2.3
7$^-$	−540.29648	−540.37816	0.21273	359.3	–				
8a	−194.16109	−194.16369	0.09798			39.2	18.2	18.0	0.2
8a$^-$	−193.58481	−193.67855	0.08359	354.1	353.6 ± 1.3				
8b	−656.40558	−656.41403	0.27001			31.0	12.8	14.3	1.5
8b$^-$	−655.85716	−655.94182	0.25542	336.5	337.7 ± 2.1				
9a	−347.86033	−347.86417	0.14825			42.9	20.7	20.1	0.6
9a$^-$	−347.28728	−347.37277	0.13345	351.8	351.9 ± 2.1				
9b	−387.19180	−387.19575	0.17780			45.4	22.3	21.8	0.5
9b$^-$	−386.61555	−386.70020	0.16278	353.7	–				
9c	−387.19187	−387.19633	0.17787			47.1	23.4	22.5	0.9
9c$^-$	−386.61448	−386.69814	0.16289	354.4	–				
9d	−578.97874	−578.98649	0.23417			37.4	17.0	17.3	0.3
9d$^-$	−578.42046	−578.50418	0.21966	342.7	–				
10a	−501.55829	−501.56556	0.19832			46.6	23.1	22.6	0.5
10a$^-$	−500.98549	−501.06800	0.18320	351.4	351.7 ± 2.1				
10b	−593.81857	−593.82809	0.19877			26.4	9.8	8.3	1.5
10b$^-$	−593.29060	−593.36393	0.18493	324.1	321.4 ± 2.0				
11	−733.86335	−733.87028	0.30731			58.4	30.9	30.6	0.3
11$^-$	−733.28517	−733.35338	0.29168	354.5	358.7 ± 2.2				
12	−40.53486	−40.53493	0.04901			92.6	53.5	56.0	2.5
12$^-$	−39.85416	−39.96183	0.03168	417.7	418.0 ± 3.5				
13	−348.98763	−348.99107	0.17089			27.7	10.6		
13$^-$	−348.44225	−348.52607	0.15819	335.7					
14a	−1179.28478	−1179.34587	0.17178			−10.7	−14.8		
14a$^-$	−1178.85989	−1178.94172	0.15886	260.0					

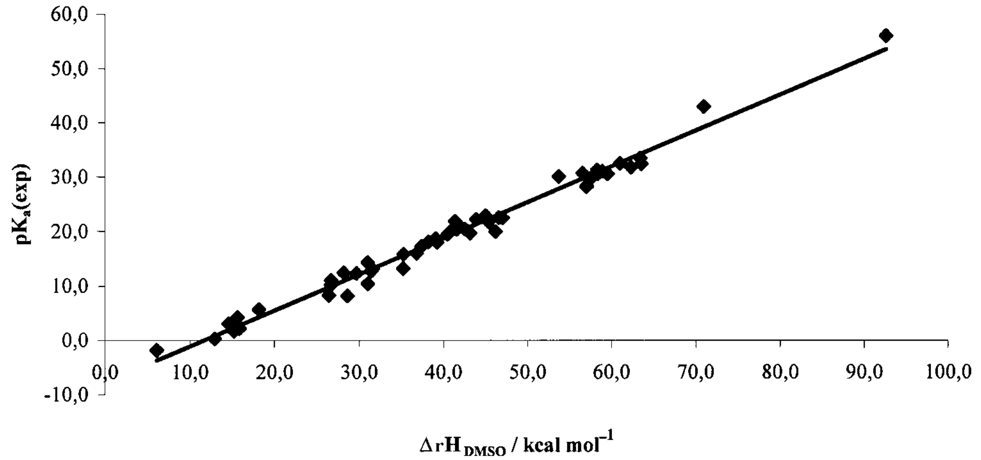
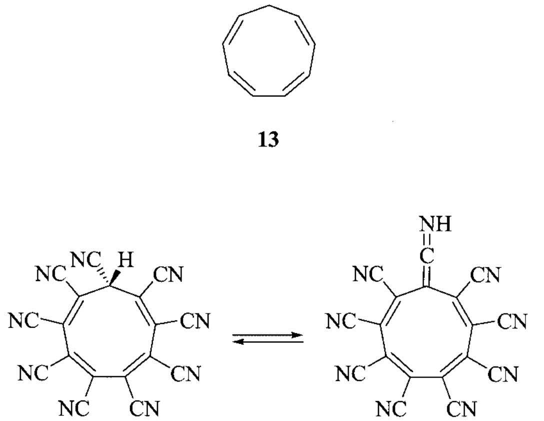


Figure 3. Linear relationship between Δ_rH_{DMSO} and available experimental pK_a(exp) values for the organic acids given in Table 1

pounds. The largest change upon deprotonation is found in the carbon−carbon bonds closest to the parent C(sp^3) nucleus, where the bond lengths are shorter by 0.1 Å. It is worth mentioning that both neutral acid **14a** and its deprotonated form **14a**$^-$ are non-planar, the latter possessing C_2 symmetry. The reason for the non-planarity of **14a**$^-$ is the steric requirements of the accumulated CN substituents. The non-planarity of **14a**$^-$ and the extremely high acidity of **14a** indicate that the anionic resonance is more important than aromatization of the nine-membered ring in the anion. We note in passing that the planar D_{9h} form of **14a**$^-$ is 21.4 kcal·mol^{-1} less stable, as calculated by the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) model.

Conclusion

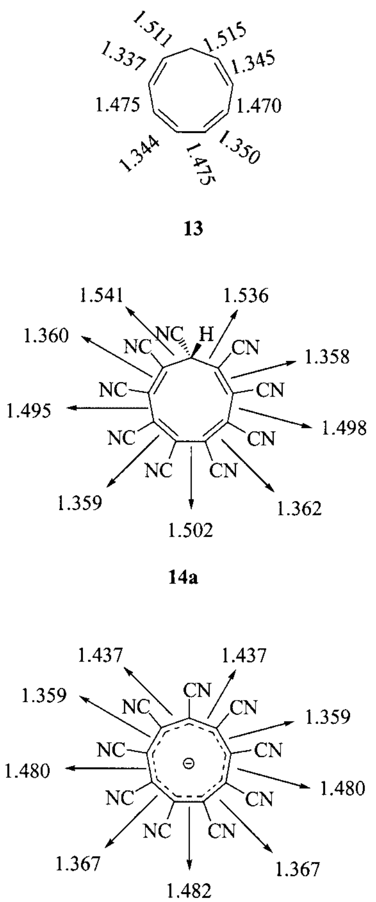
It has been shown that the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) model represents a very good compromise between practicality and reliability in predicting the acidity of CH acids in the gas phase and DMSO. Thus, the theoretically predicted proton affinities of the corresponding



13

14a **14b**

Figure 4. Cyclononatetraene (**13**) and the prototropic tautomers **14a** and **14b**

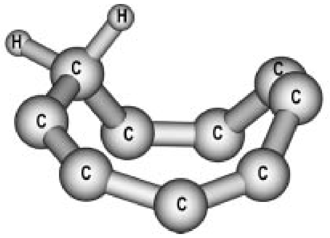


13

14a

14a–

Figure 5. Selected carbon−carbon bond lengths obtained at the B3LYP/6-31G(d) level of theory (in Å)



Scheme 1. Nonplanarity in cyclononatetraene **13** (only sp^3 hydrogens are shown)

conjugate bases can safely be used as good estimates of the true values in systems where the measured data are not available. This is of particular importance for systems not amenable to experiments. It has also been found that there is a good linear relationship between the enthalpies of the proton-transfer reactions in DMSO and the observed pK_a(exp) values. By using this relation, the acidities of the parent cyclononatetraene **13** and its nonacyano derivative **14a** are predicted. The corresponding pK_a values are 10.6 and −14.8, respectively. It appears that **14a** is a very powerful neutral superacid. The origin of its highly pronounced acidity has been identified as a strong anionic resonance in the resulting conjugate base. Since the anion **14a**$^-$ is nonplanar, it follows that the anionic resonance dominates over the aromatization of the nine-membered ring, in contrast to the parent molecule **13**, where a perfect aromatization in the conjugate base **13**$^-$ is found.

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