In Search of Ultrastrong Brønsted Neutral Organic Superacids: A DFT Study on Some Cyclopentadiene Derivatives

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Abstract: An efficient but reasonably accurate B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) computational procedure showed that pentasubstituted cyclopentadienes such as (**C**N)$_5$C$_5$H, (NO$_2$)$_5$C$_5$H, and (**N**C)$_5$C$_5$H containing strongly electron-withdrawing groups are neutral organic superacids of unprecedented strength. The boldface denotes the atom attached to the cyclopentadiene framework. All of them exhibit prototropic tautomerism by forming somewhat more stable structures with C=NH, NO$_2$H, and N=CH exocyclic fragments, respectively. The acidity (ΔH_{acid}) of these is lower, but only to a rather small extent. The ΔH_{acid} enthalpies of these last three tautomers are estimated to be 271, 276, and 282 kcal mol^{-1}, respectively. Hence, the most stable tautomers of (**C**N)$_5$C$_5$H and (**N**C)$_5$C$_5$H represent a legitimate target for synthetic chemists. On the other hand, (NO$_2$)$_5$C$_5$H is less suitable for practical applications, because of its high energy density. The origin of the highly pronounced acidity of these compounds was analyzed by using the recently developed triadic formula. It is found that very high Koopmans' ionization energy $(\text{IE})_n^{\text{Koop}}$ of conjugate bases exerts a decisive influence on acidity. It follows as a corollary that the overwhelming effect leading to very high acidity is due to the properties of the final state. An alternative picture is offered by homodesmotic reactions, wherein the cyclic systems are compared with their linear counterparts. It is found that the acidity of cyclopentadiene (**CP**) is a consequence of aromatic stabilization in the **CP**$^-$ anion. The extreme acidity of pentacyanocyclopentadiene (**C**N)$_5$C$_5$H is due to aromatization of the five-membered ring and a strong anionic resonance effect in the resultant conjugate base. The neutral organic superacids predicted by the present calculations may help to bridge the gap between existing very strong acids and bases.

Keywords: acidity · aromaticity · density functional calculations · substituent effects · superacidic systems

Introduction

According to widespread usage, acidity in the Brønsted sense is the ability of a substance to lose a proton and to accommodate the resulting negative charge. Design and synthesis of strong acids have received considerable attention, because the generated protons and anions can participate in a variety of important and useful chemical transformations. They are indispensable reagents in organic syntheses[1] and in industrial catalysis.[2] Strong superacids are pivotal in so-called general acid catalysis, in which the rate is accelerated not only by an increase in solvent H$^+$ ions, but also by an increase in the concentration of other (super)acids that exert a catalytic activity. In this type of catalysis the strongest acids are the best catalysts.[3] It is noteworthy in this respect that Brønsted acids are sometimes better catalysts than their comparable Lewis counterparts;[4] alternatively, they can act in a complementary way.[5] Hence, much effort has been devoted to tailoring new acids and superacids.[6–12] Two strategies deserve particular attention. In the first, the characteristic groups exhibiting appreciable intrinsic acidity (CH, NH, OH, or SH) are identified and subsequently enhanced by deliberately selected affixed groups or substituents with highly delocalizd charge. The latter leads to favorable field, inductive, and/or π-resonance effects.[9] The second approach is based on Yagupolskii's concept of the electron superacceptor substituents, exemplified by =NSO$_2$F and

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

DOI: 10.1002/chem.200400337

=NSO_2CF_3, which by replacing an oxygen atom doubly bonded to an S, P, or I atom form very strong superacids.[10–12] The rationale for the extraordinarily high acidities is found in electronic and structural relaxation of the resulting anions, which are stabilized by resonance because of the extended conjugated π systems formed by the molecular backbone and superacceptor groups placed at suitable positions. This is in harmony with the interpretation of acidity offered by the triadic formula,[13] which shows that the higher the ionization energy of the conjugate base, as estimated within the approximation of Koopmans' theorem, the higher the acidity. Large $\mathrm{IE}^{\mathrm{Koop}}$ ionization energies are found in particular in anionic conjugate bases, characterized as a rule by strong resonance or aromatic stabilization of the anion upon deprotonation of the parent acid. It follows that properties of the final state are of pivotal importance. This knowledge gives a useful hint for constructing strong neutral organic superacids, which should be sought and found in systems undergoing pronounced anionic aromatization after proton cleavage. For example, it is known that cyclopentadiene (**CP**) is a rather acidic hydrocarbon ($pK_a \approx 16$), which is attributed to the aromatic character of its corresponding carbanion.[14] The goal of this computational work is to show that some cyano derivatives of cyclopentadiene are ultrastrong superacids. The precursor cyclopentadiene is easily produced by petroleum cracking processes,[15] and all possible cyanocyclopentadienes can be prepared by stepwise cyanation of cyclopentadiene with cyanogen chloride.[6] We expect that other highly substituted cyclopentadiene derivatives could be prepared without great difficulties, too. To get an idea about the effect of various electron-withdrawing substituents located at the C(sp^3) carbon atoms in **CP**, we first examine intrinsic acidity of some C(sp^3) systems par excellence, namely, mono- and polysubstituted methanes, which do not exhibit aromatic stabilization upon deprotonation. Hence, they provide suitable reference systems for evaluating the effects of aromaticity on the acidity of various cyclopentadiene derivatives.

Abstract in Croatian: *Primjenom B3LYP/6-311+G(d,p)// B3LYP/6-31G(d) metode pokazano je da organski spojevi poput pentasupstituiranih ciklopentadiena* $(\mathbf{C}N)_5C_5H$, $(NO_2)C_5H$ *i* $(\mathbf{N}C)_5C_5H$ *pokazuju izuzetno veliku kiselost usljed djelovanja jakih elektron-akceptorskih grupa. Važno je istaknuti da su najstabilniji oblici ovih spojeva prototropni tautomeri, koji posjeduju C=NH,* NO_2H *i N=CH egzociklične fragmente. Njihova kiselost je nešto manja od tautomera, koji posjeduju C(sp^3) ugljikov atom. Unatoč tome, njihove entalpije* ΔH_{acid} *su 271, 276 i 282 kcal mol*$^{-1}$*, što znači da se radi o rekordno jakim superkiselinama. Uzrok ovako visoke kiselosti supstituiranih ciklopentadiena analiziran je primjenom nedavno razvijene trihotomske formule. Ustanovljeno je da dominantan utjecaj ima Koopmansova ionizacijska energija* $(IE)_n^{Koop}$ *konjugiranih baza nastalih deprotoniranjem. No znatan doprinos kiselosti daje i aromatizacija peteročlanog prstena i vrlo jaka anionska rezonancija u konjugiranim bazama. Možemo, dakle, zaključiti da su superkisela svojstva spomenutih supstituiranih ciklopentadiena posljedica karakteristika konačnog stanja. Sinteza ovih spojeva pridonijet će stvaranju zajedničke ljestvice superkiselina i superbaza.*

Theoretical Framework

Acidity is given by the enthalpy change ΔH_{acid} for Equation (1), which is calculated according to Equation (2), where ΔE_{acid} is the change in the total energy of the participants of reaction (1), which includes the zero-point energy and the finite temperature (298.15 K) correction, and $\Delta(pV)$ the pressure–volume term.

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

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

Stronger acids have smaller numerical values of ΔH_{acid} that imply easier release of the proton. A theoretical model providing a very good compromise between reliability (accuracy) and practicality (feasibility) is the DFT-B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) approach, hereafter denoted as B3LYP. It gives acidities which compare reasonably well with experiment and with more accurate, but much more computationally demanding G2 or G2(MP2) methods.[16–20] This conclusion is supported by the very good performance of the DFT-B3LYP approach in reproducing electron affinities.[21–23]

A useful tool for interpretation of acidities is embodied in the triadic formula[13] [Eq. (3)], which describes protonation of the conjugate base anion $\mathrm{A^-}$, in other words a reverse deprotonation reaction.

$$\mathrm{PA(A^-)}_\alpha = -\mathrm{IE(A^-)}_n^{\mathrm{Koop}} + E(\mathrm{ei})_{\mathrm{rex}}^{(n)} + (\mathrm{BDE})^{\cdot}_{\alpha} + 313.6\,\mathrm{kcal\,mol^{-1}} \tag{3}$$

The site of protonation is denoted by α, and $\mathrm{IE(A^-)}_n^{\mathrm{Koop}}$ is the *n*th Koopmans' ionization energy of the anion calculated in the frozen electron density and clamped atomic nuclei approximation (i.e., ionization from the *n*th orbital, counting the HOMO as the 1st). The reorganization effect following electron ejection by ionization of the anion is given by the relaxation energy $E(\mathrm{ei})_{\mathrm{rex}}^{(n)}$, defined by Equation (4).

$$E(\mathrm{ei})_{\mathrm{rex}}^{(n)} = \mathrm{IE(A^-)}_n^{\mathrm{Koop}} - \mathrm{IE(A^-)}_1^{\mathrm{ad}} \tag{4}$$

Finally, the bond dissociation energy describing homolytic C−H scission in the deprotonation process at position α is given by the term $(\mathrm{BDE})^{\cdot}_{\alpha}$. The above procedure is a simple extension of the thermochemical cycle, where a sum of $-\mathrm{IE(A^-)}_n^{\mathrm{Koop}}$ and $E(\mathrm{ei})_{\mathrm{rex}}^{(n)}$ is replaced by a single term $-\mathrm{IE(A^-)}_1^{\mathrm{ad}}$. However, inclusion of the Koopmans' ionization energy has interpretative advantages, because it mirrors the effect of the final state, or, in other words, it reflects the frozen electronic structure of the conjugate bases. Moreover, in contrast to the first adiabatic ionization energy $\mathrm{IE(A^-)}_1^{\mathrm{ad}}$ occurring in the thermochemical cycle, $\mathrm{IE(A^-)}_n^{\mathrm{Koop}}$ corresponds to the *n*th ionization energy, which is related to a specific MO that is most affected by protonation. Thus, it is closely associated with the site of the anion that is protonated. In the case of a lone pair localized on the atom under proton attack, it is the molecular orbital describing this lone pair. Identification of such MOs is usually unambiguous and poses no problem. Triadic Equation (3) is exact and the errors in calculating PAs stem from the approximate estimates of the three terms appearing in its mathematical expression. The triadic analysis applied here is executed at the G2(MP2) level of theory, whereas Koopmans' ionization energies are calculated by the restricted HF/6-311+G(3df,2p)//MP2(full)/6-31G(d) model in accordance with the proposed procedure.[13] Bond dissociation energies are obtained by use of the unrestricted G2(MP2) approach. The G2(MP2) computational scheme gives results of high accuracy, but its application is restricted to rather small systems. For this reason we performed triadic analysis in polysubstituted cyclopentadienes at the lower B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level. As discussed by Deakyne recently,[24] the triadic analysis proved a superior approach for interpreting basicity and acidity than other models developed and used earlier.

All calculations were carried out by employing the Gaussian98 suite of programs.[25]

Results and Discussion

Substituted methanes: To obtain some insight into the role of various substituents in determining acidity of cyclopentadiene derivatives, we examined their influence in substituted methanes CH_3R and CHR_3, where R = H, **C**N, NO_2, **N**C, F, Cl, and Br. Here, boldface denotes the atom attached to the cyclopentadiene or methane framework. The substituted methanes serve as species with paradigmatic sp^3 carbon centers, which in turn are of central importance in our family of target compounds, substituted cyclopentadienes. Therefore, let us consider the monosubstituted methanes first (Table 1).

Table 1. Acidities of some substituted methanes as calculated by the B3LYP/6-311 + G(d,p)//B3LYP/6-31G(d) method (in kcal mol^{-1}). They are compared with the G2(MP2) and experimental estimates for monosubstituted methanes.[a]

R	CH_3R	B3LYP ΔH_{acid}	G2(MP2) ΔH_{acid}	Exptl ΔH_{acid}	CHR_3	B3LYP ΔH_{acid}	G2(MP2) ΔH_{acid}	Exptl ΔH_{acid}
H	CH_4	418.2	418.1	418.0 ± 3.5				
F	CH_3F	407.7	410.7	409.0 ± 4.0	CHF_3	373.6	380.5	378.0 ± 1.4
Cl	CH_3Cl	395.8	397.7	396.0 ± 3.1	$CHCl_3$	354.7	360.0	357.6 ± 2.1
Br	CH_3Br	391.4	393.8	392.7 ± 3.1	$CHBr_3$	347.4	352.8	349.7 ± 2.2
NC	CH_3**N**C	381.3	383.8	380.6 ± 2.1	CH(**N**C)$_3$	321.6	329.0	
CN	CH_3**C**N	371.7	374.9	374.8 ± 2.0	CH_2(**C**N)$_2$	329.5	335.6	335.8 ± 2.1
					CH(**C**N)$_3$	294.4	302.4	
NO_2	CH_3NO_2	353.1	357.8	358.0 ± 5.0	$CH(NO_2)_3$	303.4	314.8	

[a] Experimental ΔH_{acid} values are taken from [26].

Agreement between the B3LYP/6-311 + G(d,p)//B3LYP/6-31G(d) results, G2(MP2) values, and experimental data is reasonably good. Whereas the G2(MP2) method generally gives acidities within the experimental error bars, the DFT data are systematically lower than the ab initio results by about 3 kcal mol^{-1} for a single electronegative substitute, and this implies that the general trend is reproduced well for the CH_3R set of compounds and that quite reliable ΔH_{acid} values are obtained by adding this offset value. The offset correction should be increased to 6–7 kcal mol^{-1} for triply substituted methanes, that is, the error is roughly proportional to the number of substituents (Table 1). The calculated B3LYP/6-311 + G(d,p)//B3LYP/6-31G(d) ΔH_{acid} values correctly reproduce the trend of changes. It is noteworthy that, by taking into account the offset corrections, one obtains useful acidity estimates for electron-rich substituted methanes at the B3LYP level.

Counterintuitively, acidity increases along the series CH_3R (R = F, Cl, Br), although the electronegativity of the halogen atoms decreases. One is tempted to rationalize results in terms of properties of the free atoms first. However, it would be erroneous to try to explain the increase in acidity with the electron affinities of the free (i.e., atomic) halogens. Our G2(MP2) and [B3LYP/6-311 + G(d,p)//B3LYP/6-31G(d)] calculations of the electron affinities (EA) of F, Cl, and Br atoms yield 79.5 [80.4], 83.5 [85.9], and 79.6 [82.9 kcal mol^{-1}], respectively, that is, the EA is increased in the Cl relative to the F atom, but decreases again for Br, which assumes a value similar to that of F. Hence, the atomic EAs do not exhibit monotonic behavior and cannot explain the high acidity of CH_3Br. The electrophilicity index ω_{gs}, which measures the electrophilic power of a substituent, introduced by Parr et al.[27] recently, is not helpful either. The electrophilicity indices ω_{gs} for free F, Cl, and Br atoms in their ground states are 3.86, 3.67, and 3.40 eV, respectively, a trend opposite to that found for acidity of CH_3R (R = F, Cl, Br). Analysis of atomic charges obtained by the Löwdin partitioning technique[28] reveals that F, Cl, and Br atoms in FCH_2^-, $ClCH_2^-$, and $BrCH_2^-$ anions have nearly equal values of -0.48, -0.51, and -0.51 $|e|$, respectively. Therefore, they are also not useful in rationalizing the trend of acidity.

The effect of particular substituents on acidity is best understood in terms of three contributions provided by the triadic analysis [Eq. (3)], as summarized in Table 2. It is useful to examine variations of the three terms entering Equation (3) from their reference values defined by a gauge molecule. In the case of substituted methanes this is the parent CH_4. Consequently, a change in acidity induced by substituent R is succinctly given by a triad of values $[\Delta(-\mathrm{IE}_n^{\mathrm{Koop}}), \Delta E(\mathrm{ei})_{\mathrm{rex}}^{(n)}, \Delta(\mathrm{BDE})^{\cdot}_{\alpha}]_{\mathrm{R}}$, where $\Delta(-\mathrm{IE}_n^{\mathrm{Koop}}) = -\mathrm{IE}(CH_2R^-)_n^{\mathrm{Koop}} + \mathrm{IE}(CH_3^-)_n^{\mathrm{Koop}}$, $\Delta E(\mathrm{ei})_{\mathrm{rex}}^{(n)} = E(\mathrm{ei})_{\mathrm{rex}}^{(n)}(CH_2R^-) - E(\mathrm{ei})_{\mathrm{rex}}^{(n)}(CH_3^-)$, and $\Delta(\mathrm{BDE})^{\cdot}_{\alpha} = (\mathrm{BDE})^{\cdot}_{\alpha}(CH_2R^-) - (\mathrm{BDE})^{\cdot}_{\alpha}(CH_3^-)$. More precisely, the substituent effect is obtained by $\mathrm{PA}(CH_2R^-) - \mathrm{PA}(CH_3^-) = \Sigma[\Delta(-\mathrm{IE}_n^{\mathrm{Koop}}), \Delta E(\mathrm{ei})_{\mathrm{rex}}^{(n)}, \Delta(\mathrm{BDE})^{\cdot}_{\alpha}]_{\mathrm{R}}$, where the summation sign signifies addition of the three terms in brackets. We

Table 2. Triadic analyses of proton affinities of conjugate bases CH_2R^- (R = H, F, Cl, Br, **N**C, **C**N, NO_2) and CR_3^- (R = F, Cl, Br, **C**N) obtained by applying the G2(MP2) method and Equation (3). All terms are given in kcal mol^{-1}.[a,b]

Anion	$(\mathrm{IE})_n^{\mathrm{Koop}}$	$(\mathrm{IE})_1^{\mathrm{ad}}$	$E(\mathrm{ei})_{\mathrm{rex}}^{(n)}$	$(\mathrm{BDE})^{\cdot}_{\alpha}$	PA(anion)
CH_3^-	$(25.2)_1$	1.3	23.9	105.8	418.1
CH_2F^-	$(42.8)_1$	5.6	37.2	102.7	410.7
CH_2Cl^-	$(58.9)_1$	16.8	42.1	100.9	397.7
CH_2Br^-	$(66.2)_1$	21.9	44.3	102.1	393.8
CH_2**N**C$^-$	$(41.7)_1$	27.1	14.6	97.3	383.8
CH_2**C**N$^-$	$(49.8)_1$	36.7	13.1	98.0	374.9
$CH_2NO_2^-$	$(73.0)_1$	57.8	15.2	102.0	357.8
CF_3^-	$(97.2)_1$	41.2	56.0	108.1	380.5
CCl_3^-	$(97.1)_1$	48.6	48.5	95.0	360.0
CBr_3^-	$(104.0)_1$	55.6	48.4	94.8	352.8
CH(**C**N)$_2^-$	$(78.5)_1$	68.6	9.9	90.6	335.6
C(**C**N)$_3^-$	$(107.3)_1$	94.5	12.8	83.3	302.4

[a] Koopmans′ ionization energies $(\mathrm{IE})_n^{\mathrm{Koop}}$ correspond to HF/6-311 + G(3df,2p)//MP2(full)/6-31G(d) calculations. Other data were obtained by the restricted closed-shell G2(MP2) method, except for the homolytic bond dissociation energy $(\mathrm{BDE})^{\cdot}_{\alpha}$, which was calculated within the unrestricted G2(MP2) approach. [b] $(\mathrm{IE})_n^{\mathrm{Koop}}$ and $(\mathrm{IE})_1^{\mathrm{ad}}$ are Koopmans′ nth and the first adiabatic ionization energies, respectively.

shall omit the summation sign hereafter for the sake of simplicity. The influence of the halogen atoms on the acidity in CH_3R (R = F, Cl, Br) is described by triads $[-17.6, 13.3, -3.1]_F = -7.4$, $[-33.7, 18.2, -4.9]_{Cl} = -20.4$, and $[-41.0, 20.4, -3.7]_{Br} = -24.3$ kcal mol^{-1}, respectively. It appears that the bond dissociation energy decreases along the series and thus increases the acidity of methyl halides by 3–5 kcal mol^{-1}. However, a decisive influence on the enhanced acidity is exerted by the Koopmans' ionization energies, which in turn surpass the positive contributions of the term leading to a decrease in PA(A^-) by −4.3, −15.5, and −20.6 kcal mol^{-1} for F, Cl, and Br substituents, respectively, and thus increase CH_3R (R = F, Cl, Br) acidities. Since Koopmans' ionization energies mirror properties of the final state in the deprotonation process, it follows that enhanced acidity in methyl halides is a consequence of a better accommodation of the negative charge and lower HOMO orbital energy in conjugate bases than in the CH_3^- ion. This finding deserves further comment.

The analysis of HOMOs reveals that they are composed of the antibonding combination of the hybrid orbital of the C atom and the properly oriented p orbital of the halogen atom. First, HOMO orbital energies decrease relative to that in unsubstituted CH_3^-, since halogen atoms increase the formal positive charge on the C atom and thus stabilize its lone pair. Second, the antibonding character due to opposite phases of AOs decreases along the series because the overlap between C and X atomic AOs decreases for two reasons: 1) the C–X (X = F, Cl, Br) bond length increases from 1.520 to 2.198 Å, and 2) the disparity in the size of the AOs sharply increases for the large Cl and Br atoms. Comparable size of AOs is a prerequisite for efficient overlap. It follows that HOMOs should have lower orbital energies as the size of the halogen atom increases. This finding is of some significance, since it is common to interpret acidity of methyl halides in terms of the polarizability of the halide atoms. The latter are reflected in the relaxation energy $E(\mathrm{ei})_{\mathrm{rex}}$, which increases along the series CH_3R (R = F, Cl, Br). The present analysis shows, however, that acidity is predominantly a consequence of the composition of the HOMOs of the conjugate bases.

Substantial enhancement of acidity of substituted methanes is further found for **C**N and NO_2 groups, as evidenced by ΔH_{acid} values of 374.9 and 357.8 kcal mol^{-1}, respectively. The triply substituted CHR_3 compounds exhibit roughly linear increases in acidity with increasing number of substituents in all cases with the notable exception of $CH(NO_2)_3$. This compound is considerably less acidic than expected by linear extrapolation. As a consequence, the hierarchy of acidity is changed, and $CH(\mathbf{C}N)_3$ is the most acidic triply substituted methane derivative. The reason for behaviour is that the nitro group is sterically highly demanding. Consequently, the overcrowded $CH(NO_2)_3$ system cannot form a totally planar carbanion upon deprotonation, which would enable optimal resonance (see below). Hence, attenuation of its acidity is not surprising. In contrast, the anion $[C(\mathbf{C}N)_3]^-$ exhibits a very favourable resonance effect due to three equivalent (and hence degenerate) resonance structures. Its spatial structure is perfectly planar with D_{3h} symmetry and rather short C–C bonds. Hence, **C**N is the most convenient substituent, since it combines two advantageous features: a pronounced electron-withdrawing effect and moderate spatial requirements. Consequently, we focus mainly on $CH(\mathbf{C}N)_3$ and consider other compounds for the sake of comparison. The $(\mathrm{BDE})^{\bullet}_{\alpha}$ values for formation of radicals decrease in the order $(\mathbf{C}N)CH_2^{\bullet}$, $(\mathbf{C}N)_2CH^{\bullet}$, and $(\mathbf{C}N)_3C^{\bullet}$ (98.0, 90.6, and 83.3 kcal mol^{-1}, respectively), presumably because the central carbon atom becomes more electron deficient as the number of cyano groups increases, which weakens its bonding capacity. Triadic analysis $[-82.1, -11.1, -22.5] = -115.7$ shows that the influence of the highly pronounced stability of the HOMO in the conjugate base $C(\mathbf{C}N)_3^-$ is undoubtedly overwhelming in determining the acidity of $(\mathbf{C}N)_3CH$. However, it turns out that its high acidity is a result of the concerted action of all three effects. The contributions of the relaxation effect and bond dissociation energy are significantly smaller, but they are by no means negligible.

It is of interest to compare relative acidities of $CH(\mathbf{C}N)_3$ and $CH(NO_2)_3$. A useful tool is provided by isodesmic reactions,[29] which involve the same number of atoms of the participating elements in the reactants and products, as well as the same number of single, double, and triple bonds. The relevant reactions read as in Equations (5) and (6), where $E(\mathrm{intf.})_1$ and $E(\mathrm{intf.})_2$ are the interference energies in $CH(\mathbf{C}N)_3$ and $CH(NO_2)_3$ describing intramolecular interactions between **C**N and NO_2 groups, respectively.

$$CH(\mathbf{C}N)_3 + 2\,CH_4 \rightarrow 3\,CH_3CN + E(\mathrm{intf.})_1 \tag{5}$$

$$CH(NO_2)_3 + 2\,CH_4 \rightarrow 3\,CH_3NO_2 + E(\mathrm{intf.})_2 \tag{6}$$

They are $E(\mathrm{intf.})_1 = 21.4$ kcal mol^{-1} and $E(\mathrm{intf.})_2 = 17.9$ kcal mol^{-1}, as obtained with the G2(MP2) method. The positive sign shows that substituents repel each other and that this unfavorable interaction is 3.5 kcal mol^{-1} larger in $CH(\mathbf{C}N)_3$. On the other hand the stabilizing anionic resonance effect is considerably larger in $C(\mathbf{C}N)_3^-$ than in $C(NO_2)_3^-$, as revealed by isodesmic reactions [Eq. (7) and (8)].

$$C(\mathbf{C}N)_3^- + 2\,CH_4 \rightarrow CH_2CN^- + 2\,CH_3\mathbf{C}N + E(\mathrm{res})_1^- \tag{7}$$

$$C(NO_2)_3^- + 2\,CH_4 \rightarrow CH_2NO_2^- + 2\,CH_3NO_2 + E(\mathrm{res})_2^- \tag{8}$$

The corresponding resonance energies $E(\mathrm{res})_1^-$ and $E(\mathrm{res})_2^-$ of −51.0 and −25.1 kcal mol^{-1}, respectively, imply that anionic resonance in $C(\mathbf{C}N)_3^-$ is stronger by 25.9 kcal mol^{-1}. Combination of Equations (5)–(8) yields Equation (9).

$$\begin{aligned}\Delta H_{\mathrm{acid}}[CH(NO_2)_3] - \Delta H_{\mathrm{acid}}[CH(\mathbf{C}N)_3] \\ = \Delta H_{\mathrm{acid}}[CH_3NO_2] - \Delta H_{\mathrm{acid}}[CH_3\mathbf{C}N] \\ + [E(\mathrm{res})_2^- - E(\mathrm{res})_1^-] + [E(\mathrm{intf.})_1 - E(\mathrm{intf.})_2]\end{aligned} \tag{9}$$

It follows that both the increased intramolecular repulsion in the initial acids (3.5 kcal mol^{-1}) and the resonance effect (25.9 kcal mol^{-1}) in the corresponding conjugate bases contribute to the increased acidity of $CH(\mathbf{C}N)_3$ relative to $CH(NO_2)_3$. However, the latter effect is considerably more important; it is larger by a factor of seven.

Furthermore, triadic analysis is helpful in pinpointing imperfections of the B3LYP method in reproducing acidity. Let us denote deviation of B3LYP estimates from the more accurate G2(MP2) results as $\delta(\mathrm{B3LYP})_{\mathrm{error}} = \Delta H_{\mathrm{acid}}(\mathrm{B3LYP}) - \Delta H_{\mathrm{acid}}[\mathrm{G2(MP2)}]$. Resolving $\delta(\mathrm{B3LYP})_{\mathrm{error}}$ into three components, one obtains for CHF_3, $CHCl_3$, $CHBr_3$, $CH_3\mathbf{C}N$, and $CH(\mathbf{C}N)_3$ the following data: $[-3.6, -0.4, -3.0] = -7.0$, $[-12.0, 9.0, -2.5] = -5.5$, $[-3.6, 1.2, -3.1] = -5.5$, $[2.4, -1.5, -4.3] = -3.4$, and $[0.7, 0.7, -9.5] = -8.1$, respectively. It appears that the origin of errors in B3LYP results differs for different compounds, but their sum is roughly constant for the triply substituted methanes. Since our substituent of choice is $\mathbf{C}N$, it is useful to observe that the largest contribution to the error of $\Delta H_{\mathrm{acid}}(\mathrm{B3LYP})$ in $CH_3\mathbf{C}N$ and $CH(\mathbf{C}N)_3$ comes from the $(\mathrm{BDE})^{\cdot}_{\alpha}$ term. This error depends on the number of CN groups attached to the same carbon atom (vide infra).

Prototropic tautomerism does not affect the acidity of the substituted methanes studied here, because tautomeric species involving the hydrogen atom bonded to heteroatoms in $\mathbf{C}N$, $\mathbf{N}C$, and NO_2 groups are considerably less stable. The opposite, however, occurs in substituted cyclopentadienes, and this must be taken into account in considering their acidities, as expounded in the next section.

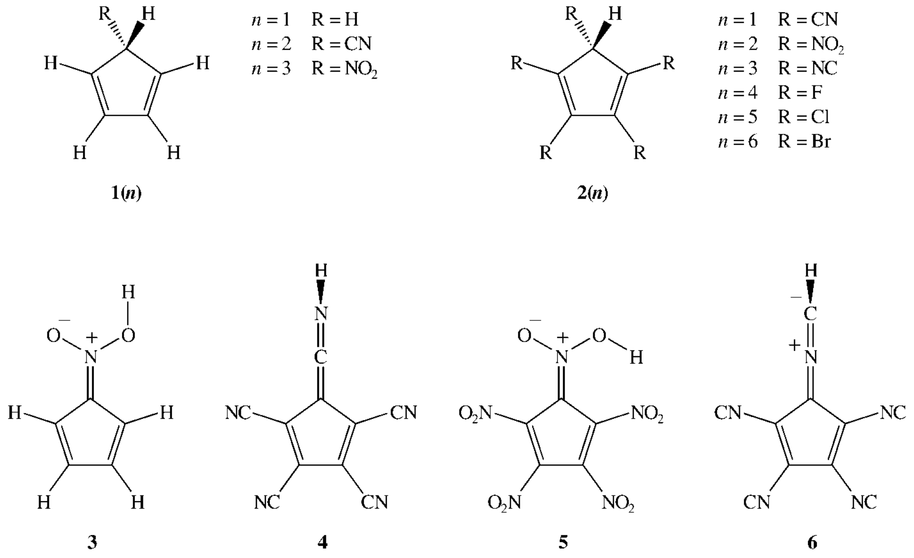
Substituted cyclopentadienes: The acidities of cyclopentadienes C_5HR_5 (R = F, Cl, Br, $\mathbf{C}N$, $\mathbf{N}C$, NO_2) and C_5H_5R (R = $\mathbf{C}N$, NO_2), depicted in Scheme 1, are summarized in Table 3.

Table 3. Acidity of cyclopentadiene and its derivatives C_5H_5R (R = H, $\mathbf{C}N$, NO_2) and C_5HR_5 (R = H, $\mathbf{C}N$, NO_2, $\mathbf{N}C$, F, Cl, Br), as obtained by the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) method (in kcal mol^{-1}).[a]

Compound	**1(1)**	**1(2)**	**1(3)**	**2(1)**	**2(2)**	**2(3)**	**2(4)**	**2(5)**	**2(6)**
ΔH_{acid}	353.5	322.2	315.9	256.5	259.4	274.5	333.4	319.8	230.6
Compound			**3**	**4**	**5**	**6**			
ΔH_{acid}			[317.4]	[263.5]	[269.4]	[275.0]			

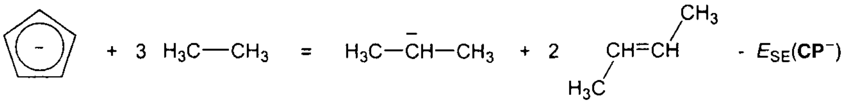
[a] Values in brackets correspond to the most stable tautomers **3**–**6** (Scheme 1).

Cyclopentadiene (**CP**) and its derivatives span a range of acidities between 256.5 and 353.5 kcal mol^{-1} according to the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) method. However, several cyclopentadiene derivatives (R = $\mathbf{C}N$, $\mathbf{N}C$, NO_2) also have prototropic tautomers. We consider only those which are more stable than the $C(sp^3){-}H$ bonded compounds **1(3)**, **2(1)**, **2(2)**, and **2(3)**. Their structures **3**–**6** are shown in Scheme 1. These tautomers have a somewhat lower acidity as a rule, with the exception of R = $\mathbf{N}C$. Nevertheless, the acidities of $C_5H(\mathbf{C}N)_5$, $C_5H(NO_2)_5$, and $C_5H(\mathbf{N}C)_5$ are still exceptionally high: the ΔH_{acid} values are 263.5, 269.4, and 275.0 kcal mol^{-1}, respectively. These extreme acidities call for rationalization. The problem of high acidity of the parent **CP** was addressed by Bordwell et al.[30] some twenty years ago. They noted that the anion $\mathbf{CP}^-$ has a π-electron stabilization energy of 2.47β according to simple Hückel theory. The resonance integral β is an adjustable parameter which can be empirically estimated by the experimental heat of hydrogenation of benzene relative to three times cyclohexene ($\Delta H_{\mathrm{hydrogenation}} = 36$ kcal mol^{-1}). Since the aromatic stabilization energy $(\mathrm{ASE})_{\mathbf{B}}$ of benzene is 2β, it straightforwardly follows that $(\mathrm{ASE})_{\mathbf{CP}^-}$ is 44.5 kcal mol^{-1}. Bordwell et al.[30] reckoned that the latter value was excessively high and tried to amend it by comparing the acidity of **CP** with that of pyrrole and open-chain model compounds. Their final conclusion was that the aromatic stabilization energy of $\mathbf{CP}^-$ should be about 24–27 kcal mol^{-1}. In view of this disparity, we felt it worthwhile to examine $(\mathrm{ASE})_{\mathbf{CP}^-}$ in more detail and compare it with the value for benzene. For this purpose we made use of both isodesmic and homodesmotic[31] reactions. The latter attempt to preserve the hybridization states of atoms in starting materials and products. Let us consider the following reactions [Eqs. (10) and (11)], where 2-butene is taken in its *trans* configuration.

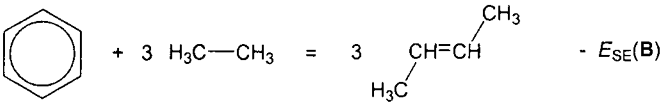


Scheme 1. Schematic representation of substituted cyclopentadienes exhibiting pronounced acidity.

Here E_{SE} is the stabilization energy, defined as a positive quantity. It should be distinguished from the aromatic stabilization energy (ASE), as the following analysis clearly shows. Athough reactions (10) and (11) preserve the number of C atoms in the formal hybridization states sp^2 and sp^2, they are only quasihomodesmotic, since the distributions of the $C(sp^3)$ and $C(sp^2)$ atoms on the left-



(10)

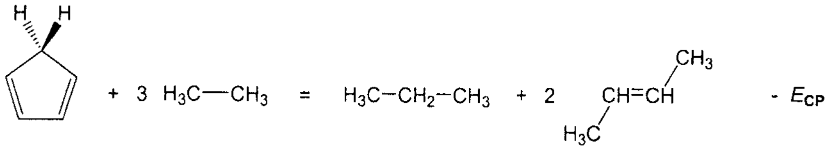


(11)

and right-hand sides are such that the number of C–C σ bonds of the same hybridization composition is not conserved. For example, taking into account that the $[CH_3CHCH_3]^-$ anion is pyramidal, one obtains in Equation (10) an imbalance in C–C$^{\sigma}$ bonds, since $3\,[C(sp^2)-C(sp^2)]^{\sigma}+[C(sp^3)-C(sp^3)]^{\sigma}\neq 4\,[C(sp^3)-C(sp^2)]^{\sigma}$. An approximate idea of this imbalance in terms of bond energies can be obtained by considering a relation between the overlap integrals of the hybrid AOs forming the σ bonds and the in situ or instantaneous bond dissociation energies (IBDEs). The latter are defined as energies required for a bond rupture, but with the formed radicals kept frozen.[32] The hybridization model gives the following IBDEs:[33] $E[C(sp^3)-C(sp^3)]=97.4$, $E[C(sp^3)-C(sp^2)]=105.8$, $E[C(sp^2)-C(sp^2)]=117.5$ kcal mol^{-1}. When these differences are taken into account, the left-hand side of Equation (10) is more stable than the right-hand side by 28.3 kcal mol^{-1}, purely due to imbalance in the C–C$^{\sigma}$ bonds, which has nothing to do with $E_{ASE}(\mathbf{CP}^-)$. Since $E_{SE}(10)_{\mathbf{CP}^-}$ is 61.8 for both G2(MP2) and B3LYP methods, it appears that $E_{ASE}(\mathbf{CP}^-)$ is roughly 33.5 kcal mol^{-1}. Note that values offered by Equations (10) and (11) are semiquantitative at best. Nevertheless, they are useful, and it is of some interest to compare them with $E_{ASE}(\mathbf{B})$ of benzene obtained by means of Equation (11). The imbalance in C–C$^{\sigma}$ bonds in this case is $3\,[C(sp^2)-C(sp^2)]+3\,[C(sp^3)-C(sp^3)]\neq 6\,[C(sp^3)-C(sp^2)]$, which implies that the left-hand side of Equation (11) is more stable by some 12 kcal mol^{-1} due to imperfect matching of the C–C$^{\sigma}$ bonds. Since $E_{SE}(\mathbf{B})$ is 32.6 and 35.8 kcal mol^{-1} according to G2(MP2) and B3LYP calculations, respectively, it follows that the aromatic stabilization of **B** is $E_{ASE}(\mathbf{B})=20.6$ or 23.8 kcal mol^{-1}, respectively. Hence, it is safe to say that $E_{ASE}(\mathbf{CP}^-) > E_{ASE}(\mathbf{B})$, which is an important result.

An interesting insight is obtained by comparing the stabilization energy $E_{SE}(\mathbf{CP}^-)$ with a triadic analysis provided by formula (3). For this purpose we make use of the data presented in Table 4, which refer to B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) calculations, because the G2(MP2) method is not applicable in heavily substituted cyclopentadienes. The $(\mathrm{IE})_1^{\mathrm{Koop}}$ of $\mathbf{CP}^-$ is 44.9 kcal mol^{-1}, and $E(\mathrm{ei})_{\mathrm{rex}}^{(n)}$ and $(\mathrm{BDE})_{\alpha}^{\cdot}$ have values of 3.9 and 80.9 kcal mol^{-1}, respectively. At first sight the $(\mathrm{IE})_1^{\mathrm{Koop}}$ value, which influences acidity the most, is surprisingly low compared to $E_{SE}(\mathbf{CP}^-)$. However, these two quantities are not directly comparable. Ionization is a single-electron event which additionally includes only the molecule in question ($\mathbf{CP}^-$). In contrast, homodesmotic reaction (10) is based on the total molecular energies and thus involves all electrons. Consequently $E_{SE}(\mathbf{CP}^-)$ reflects a collective effect. In particular, three "aromatic" π MOs of $\mathbf{CP}^-$ are protagonists of its aromatic stabilization, in contrast to single ionization from its π HOMO. Nor should one neglect the influence of the σ framework, which is inherently included in reaction (10). Furthermore, the stabilization energy of $\mathbf{CP}^-$ is obtained relative to model compound $(CH_3-CH-CH_3)^-$ by Equation (10). Hence, $E_{SE}(\mathbf{CP}^-)$ depends on the way in which the model system describes a localized anionic center. It is important to realize that $(\mathrm{IE})_1^{\mathrm{Koop}}$ mirrors intrinsic features of $\mathbf{CP}^-$ itself, whereas $E_{SE}(\mathbf{CP}^-)$ measures deviation of the stabilization energy from the more or less arbitrarily selected "ideal" gauge system.

Nevertheless, it is possible to find a direct relation between the triadic formula (3) and quasihomodesmotic reaction (10). It provides an illuminating and more detailed description of $E_{SE}(\mathbf{CP}^-)$. Consider the following [Eq. (12)].



(12)

Taking the difference between Equations (10) and (12) one obtains Equation (13).

$$\Delta H_{acid}(\mathbf{CP})-\Delta H_{acid}(\text{propane}) = -[E_{SE}(\mathbf{CP}^-)-E_{CP}] \tag{13}$$

Here, it is tacitly assumed that ΔH_{acid}(propane) refers to deprotonation of the methylene group. The B3LYP calculation yields $E_{\mathbf{CP}}=-1.1$ kcal mol^{-1}. ΔH_{acid}(propane) is 416.6 kcal mol^{-1} for cleavage of a CH_2 proton. Next, Equation (13) can be resolved by the triadic formula into three terms [Eq. (14)], where Δ implies a difference between **CP** and propane terms.

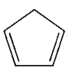
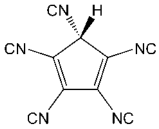
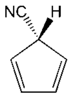
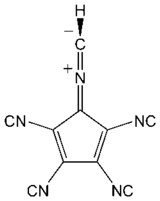
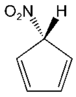
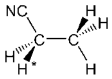
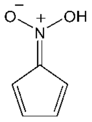
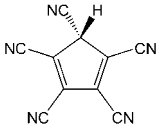
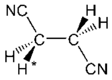
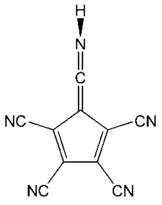
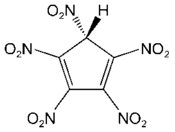
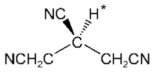
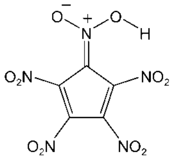
$$[\Delta(-(\mathrm{IE})_n^{\mathrm{Koop}}),\ \Delta E(\mathrm{ei})_{\mathrm{rex}}^{(n)},\ \Delta(\mathrm{BDE})_{\alpha}^{\cdot}] \tag{14}$$

More specifically, Equations (13) and (14) give Equation (15).

$$[-29.3,\ -18.4,\ -15.2] = -62.9\ \text{kcal mol}^{-1} \tag{15}$$

It follows that the HOMO is substantially stabilized in $\mathbf{CP}^-$ compared to that in the model anionic compound $(CH_3CHCH_3)^-$, and this provides the largest (29.3 kcal-

Table 4. Triadic analysis of conjugate bases of CP and some of its derivatives, calculated by the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) method (in kcal mol^{-1}).[a]

Molecule	$(\mathrm{IE})_n^{\mathrm{Koop}}$	$(\mathrm{IE})_1^{\mathrm{ad}}$	$E(\mathrm{ei})_{\mathrm{rex}}^{(n)}$	$(\mathrm{BDE})_{\alpha}^{\bullet}$	PA(anion)	Molecule	$(\mathrm{IE})_n^{\mathrm{Koop}}$	$(\mathrm{IE})_1^{\mathrm{ad}}$	$E(\mathrm{ei})_{\mathrm{rex}}^{(n)}$	$(\mathrm{BDE})_{\alpha}^{\bullet}$	PA(anion)
 **CP**	$(44.9)_1$	41.0	3.9	80.9	353.5	 **2(3)**	$(112.1)_1$	108.4	3.8	69.3	274.5
 **1(2)**	$(69.8)_1$	64.1	5.7	72.7	322.2	 **6**	$(112.1)_1$	108.4	3.8	69.8	275.0
 **1(3)**	$(83.2)_1$	71.9	11.3	74.2	315.9	 **7**	$(40.1)_1$ $[43.4]_1$	28.9 [30.7]	11.2 [12.7]	89.0 [94.7]	373.3 [377.6]
 **3**	$(183.0)_4$	71.9	111.1	75.7	317.4						
 **2(1)**	$(144.3)_1$	127.3	17.0	70.2	256.5	 **8**	$(64.1)_1$ $[66.3]_1$	49.0 [49.3]	15.1 [17.0]	91.1 [96.3]	355.7 [360.6]
 **4**	$(144.3)_1$	127.3	17.0	77.2	263.5						
 **2(2)**	$(172.1)_1$	135.8	37.0	81.6	259.4	 **9**	$(79.6)_1$ $[84.1]_1$	59.3 [58.9]	20.3 [25.2]	89.0 [93.8]	343.3 [348.5]
 **5**	$(221.5)_3$	135.8	85.7	91.6	269.4						

[a] Results obtained by the G2(MP2) method for molecules **7**–**9** are given in brackets. Deprotonation site is denoted by an asterisk.

mol^{-1}) contribution to $E_{\mathrm{SE}}(\mathbf{CP}^-)$. This is the one-electron part of the aromatic stabilization described in reaction (10). The many-body effects are embodied in trichotomy formula in the remaining two terms: the relaxation energy $E(\mathrm{ei})_{\mathrm{rex}}^{(n)}$ and homolytic bond dissociation energy $(\mathrm{BDE})_{\alpha}^{\bullet}$. The former is a genuine collective effect involving redistribution of all electrons and rearrangement of the nuclei, while the latter is essentially a two-electron interaction related to the cleaved X–H bond in question (X = C). Perhaps it is better to characterize the $(\mathrm{BDE})_{\alpha}^{\bullet}$ term as a quasi-two-electron effect, because despite the fact that X–H bonds are highly localized, their rupture triggers some geometric and electronic structure changes due to rehybridization and redistribution of the π-electron density in the ring during the homolytic dissociation process. They are mirrored in the structural and electronic features of **CP**$^-$ and **CP** and differences thereof, just as is the case for the relaxation effect, albeit to a lesser extent. The corresponding contributions of $E(\mathrm{ei})^{(n)}_{\mathrm{rex}}$ and $(\mathrm{BDE})^{\bullet}_{\alpha}$ terms to stabilization of **CP**$^-$ are 18.4 and 15.2 kcal mol^{-1}, respectively. It follows as a corollary that the homodesmotic reaction approach is equivalent to triadic analysis as far as global effects are concerned. However, the latter has a distinct advantage that the one-electron, quasi-two-electron, and collective effects are delineated and separately described in the deprotonation process.

In what follows we focus only on the triadic analyses. It is of some interest to compare acidity between **CP** and CH_4. According to triadic analysis and B3LYP results, $[-17.6, -23.7, -23.3] = -64.6$ kcal mol^{-1}, the differences in all three terms entering triadic formula (3) are of comparable importance in enhancing acidity of **CP** compared to CH_4. Employing data listed in Table 4 and adopting **CP** as a gauge molecule reveals that increased acidity in **CP** derivatives monosubstituted at C(sp^3) center by **C**N and NO_2 groups is predominantly a result of increased $(\mathrm{IE})^{\mathrm{Koop}}_n$. This is evidenced by triads $[\Delta(-(\mathrm{IE})^{\mathrm{Koop}}_n), \Delta E(\mathrm{ei})^{(n)}_{\mathrm{rex}}, \Delta(\mathrm{BDE})^{\bullet}_{\alpha}]$, which for **1(2)** and **1(3)** read $[-24.9, 1.8, -8.2]_{\mathrm{CN}} = -31.3$ and $[-38.3, 7.4, -6.7]_{\mathrm{NO_2}} = -37.6$ kcal mol^{-1}. A particularly interesting case is nitronic acid **3**, since the ejected proton corresponds to the HOMO-3 orbital., which is composed of two σ p AOs of oxygen atoms that form an antibonding combination (Figure 1), describing their in-plane lone pairs. This leads to a huge increase in $(\mathrm{IE})^{\mathrm{Koop}}_4$, which takes on a value of 183.0 kcal mol^{-1}, and a very large relaxation energy of 111.1 kcal mol^{-1}. The associated triad has the form $[-138.1, 107.2, -5.2]_{\mathbf{3}} = -36.1$ kcal mol^{-1}. It is remarkable that the acidities of **1(3)** and **3** are very close, although their spatial and electronic structures differ widely. Although the variations in the different terms entering the triadic formula are very large, they give almost the same ΔH_{acid} values. A similar situation occurs in our target compounds **2(1)** and **4**. Their $(\mathrm{IE})^{\mathrm{Koop}}_1$ and $E(\mathrm{ei})^{(n)}_{\mathrm{rex}}$ terms are the same, since the corresponding anions are identical. The only difference is found in the $(\mathrm{BDE})^{\bullet}_{\alpha}$ term, which in **4** is higher by 7 kcal mol^{-1}. A triad describing the increase in acidity of **4** compared to **CP** is given by $[-99.4, 13.1, -3.7]_{\mathbf{4}} = -90.0$ kcal mol^{-1}. Consequently, the superacidity of **4** is a consequence of the high stability of the HOMO in the $(\mathbf{C}N)_5C_5^-$ ion.

Finally, let us compare ΔH_{acid} components of the pentasubstituted **CP 4** and **C**NCH$_3$. The B3LYP calculations yield $[-96.9, 5.4, -16.5] = -108.0$ kcal mol^{-1}. Again, the influence of the final state, mirrored by the $(\mathrm{IE})^{\mathrm{Koop}}_n$ value determines the prominent acidity of **4** compared to that of **C**NCH$_3$. It follows as a general conclusion that properties of the resulting anions produced upon deprotonation are crucial.

The errors inherent in the B3LYP approach deserve comment. They are considered for model compounds **C**NH$_2$CCH$_3$ (**7**), **C**NH$_2$CCH$_2$**C**N (**8**), and **C**NH$_2$CCH**C**NCH$_2$**C**N (**9**) first. Deviations of their ΔH_{acid} values from those obtained by the rather accurate G2(MP2) method are -3.9, -4.9, and -5.2 kcal mol^{-1}, respectively. The error in estimating the acidity of **C**NH$_2$CCH**C**NCH$_2$**C**N should be comparable to that for **2(1)**. Therefore, it appears that the ΔH_{acid} value of **2(1)** predicted by the B3LYP calculations is too low by some 5 kcal mol^{-1}. A good estimate of its ΔH_{acid} would be consequently 262 kcal mol^{-1}. Taking into account the offset value of 7 kcal mol^{-1} derived from results obtained for triply substituted methanes, one arrives at conservative estimates of the acidity of **4**, **5**, and **6** of 271, 276, and 282 kcal mol^{-1}, respectively.

Structural parameters and the electron density distributions in the studied systems provide additional insight into the properties of these strong acids. Some characteristic bond lengths and Löwdin π-bond orders calculated by the B3LYP/6–31G(d) method are presented in Table S1 (Supporting Information). The parent **CP** and its anion **CP**$^-$ exhibit the expected distances and corresponding π-bond orders. The latter assume in **CP**$^-$ a value close to that in benzene (0.66) and are evenly distributed along the molecular perimeter. Monosubstitution by **C**N and NO$_2$ in **1(2)** and **1(3)**, respectively, introduces some changes in the neutral species, but the qualitative picture remains the same. A somewhat more pronounced influence of substituents is observed in **1(2)**$^-$ and **1(3)**$^-$ ions, in which C1–C2 and C3–C4 bonds have lower π-bond orders compared to **CP**–, whereas C2–C3 and C4–C5 become more localized. This is obviously a consequence of the π-resonance interaction with **C**N and NO$_2$ groups. Structural differences between prototropic tautomers **2(1)** and **4** are appreciable. The C1–C2 and C5–C1 bonds are much shorter in **4** with concomitant increase in the π-bond order due to π resonance with the C=NH fragment. Concomitantly, the C2–C3 bond is elongated and the C3–C4 bond shortened relative to those in tautomer **2(1)**. The high bond order between C1 and the *exo* C=NH group (0.63) reflects a strong π-type resonance between five-membered ring and substituent. Significant π-electron donation

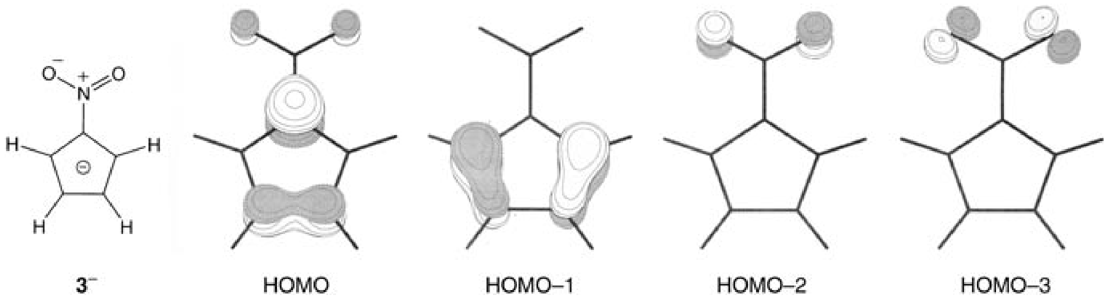


Figure 1. Four highest MOs in the $(NO_2)C_5H_4^-$ ion calculated with the HF/6-311+G(d,p)//B3LYP/6-31G(d) model.

occurs from the C=NH fragment to the ring in **4**, which shifts a portion of the nitrogen lone pair density into the aromatic moiety (vide infra). A difference in spatial structural parameters and π-bond orders between tautomers **2(2)** and **5** follows qualitatively the same pattern. They are quantitatively somewhat larger, with the consequence that **5** is better prepared for the resulting conjugate base **2(2)**$^-$. Another distinct difference is higher π-bond order between C1 and the NO_2H fragment (0.48), which indicates a stronger interaction with the ring.

The variation in the total π-electron density of the five-membered ring in neutral acids and the corresponding conjugate bases (anions), denoted Q^{π} (in $|e|$) is interesting (Table S2, Supporting Information). We find four π electrons in the ring of the parent **CP**, and six π electrons in **CP**$^-$. Monosubstitution of **CP** at C(sp^3) atoms by **C**N and NO_2 groups diminishes the π-electron charge in the rings of the respective anions, and $Q^{\pi}[\mathbf{1(2)}^-]=5.70$ and $Q^{\pi}[\mathbf{1(3)}^-]=5.56$ result. The total π-electron charge of the ring in prototropic tautomers **2(1)** and **4** indicates that the former has less than four π electrons (3.86 $|e|$), but that the latter exhibits noticeable π backdonation due to the C=NH group ($Q^{\pi}[\mathbf{4}]=4.08$). The final-state anion **2(1)**$^-$ has five planar **C**N groups that withdraw π-electron density from the ring, which results in a total π density of only 5.45 π electrons (Table S2), which is 0.55 $|e|$ less than is required for the aromatic sextet. An analogous picture is found in tautomers **2(2)**, **5**, and their common conjugate base **2(2)**$^-$. These results indicate that pentacyano-substituted **CP** in its anionic **2(1)**$^-$ form has decreased aromaticity within the five-membered ring, and yet its stabilization is larger than that in benzene due to a strong resonance effect with CN groups. This finding is conceptually important, since it shows that 1) the anionic resonance is stronger than the aromatic effect, and 2) the extraordinarily high acidity of **2(1)** is strongly affected by an interplay between aromatization and the anionic resonance.

Conclusion

We found that polysubstituted methanes bearing strongly electron withdrawing groups (F, Cl, Br, **N**C, **C**N, NO_2) exhibit increased acidity. Analysis with the triadic formula (3) reveals that the most important term influencing ΔH_{acid} values is the Koopmans' ionization energy of the final ions formed upon deprotonation. In other words, the negative charge is strongly stabilized in conjugate bases. The most acidic compound in this family is $(\mathbf{C}N)_3CH$. This is a result of a synergistic action of all three $(IE)_n^{Koop}$, $E(ei)_{rex}^{(n)}$, and $(BDE)_{\alpha}^{\bullet}$ terms. The pentasubstituted cyclopentadienes have highly pronounced acidities. Some of them, such as $(\mathbf{C}N)_5C_5H$, $(\mathbf{N}C)_5C_5H$, and $(NO_2)_5C_5H$, are candidates for superacids of unprecedented strength. The last-named is less practical, however, due to its very high energy density. Note that all three compounds exhibit prototropic tautomerism by forming more stable structures involving C=NH, NO_2H, and N=CH *exo* fragments. They have decreased acidity compared to the corresponding tautomers, but to a rather small extent. The origin of the very strong acidity of $(\mathbf{C}N)_5C_5H$, $(NO_2)_5C_5H$, and $(\mathbf{N}C)_5C_5H$ was identified as the very high ionization energy $(IE)_n^{Koop}$ of the conjugate bases and somewhat lower $(BDE)_{\alpha}^{\bullet}$ terms compared to the parent **CP**. The high $(IE)_1^{Koop}$ in **CP**$^-$ is an essential part of a general collective stabilization of this anion. This is reflected in the high stabilization energy E(SE) of **CP**$^-$, which is close to 60 kcal mol^{-1}. A simple relation connecting $E_{SE}(\mathbf{CP}^-)$ and the triadic formula was derived by considering acidity difference between **CP** and propane deprotonated at the methylene carbon atom. It turns out that $E_{SE}(\mathbf{CP}^-)=[29.3,\ 18.4,\ 15.2]-1.1=61.8\ \text{kcal mol}^{-1}$. Clearly, all three terms $(IE)_n^{Koop}$, $E(ei)_{rex}^{(n)}$, and $(BDE)_{\alpha}^{\bullet}$ act in concert, but the influence of the $(IE)_n^{Koop}$ term is the most significant. Trichotomy analysis shows that $E_{SE}(\mathbf{CP}^-)$ is a result of one-electron $(IE)_n^{Koop}$, many-electron $E(ei)_{rex}^{(n)}$, and quasi-two-electron $(BDE)_{\alpha}^{\bullet}$ effects. It is noteworthy that the aromatic stabilization of the **CP** anion $E_{ASE}(\mathbf{CP}^-)$ of 33.5 kcal mol^{-1} is larger than that in benzene ($E_{ASE}(\mathbf{B})=20.6$ kcal mol^{-1}) according to G2(MP2) calculations and homodesmotic reactions (10) and (11). An even more conceptually interesting and important finding is that the anionic resonance effect outweighs the aromaticity in pentacyano derivative $(\mathbf{C}N)_5C_5^-$ in its contribution to the very high acidity of its precursor acid. Both aromatization[34–39] and (cationic) resonance effects[40,41] play a very important role in determining basicity of neutral organic superbases. Therefore, one can safely conclude that aromatization, as well as cationic and anionic resonance in the corresponding conjugate acids and bases, are the key concepts in designing neutral organic superbases and superacids. These ideas, combined with other intrinsically highly basic functional groups such as S=N[42] and iminophosphorane[43] and new general notions such as the use of zwitterionic systems[44] or cooperative multiple intermolecular hydrogen bonding,[45] will undoubtedly close the gap which now separates the ladders of superbases and superacids.

Finally, it is concluded that the B3LYP method represents a reasonably good compromise for predicting acidities in large systems, particularly if appropriate offset corrections are applied. For example, it is estimated that the B3LYP scheme yields a ΔH_{acid} value for **2(1)** which is too low by some 5 kcal mol^{-1}, as revealed by comparison with some smaller model molecules. Hence, the best estimated ΔH_{acid} value of **2(1)** is 262 kcal mol^{-1}.

We expect that the present paper will stimulate experimental work in this field of ultrastrong neutral Brønsted superacids, in particular that it will promote syntheses of suitably substituted cyclopentadienes. We hope that theoretical methods will continue to provide help in this respect since computational chemistry is almost a mandatory tool in contemporary acid/base chemistry, at least in the gas phase, as pointed out by Yáñez et al.[19]

To summarize, the most acidic compounds studied here are **2(1)**, **4**, **2(2)**, and **5**. The last two species are more of theoretical than practical interest in view of their very high energy density and concomitant hazardous behavior, which probably preclude laboratory applications. Hence, the best candidates for highly powerful neutral organic superacids are **2(1)** and **4**.

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Received: July 19, 2004