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Carbon Acidity and Ring Strain: a Hybrid HF-DFT Approach (Becke3LYP/6-311++G**)

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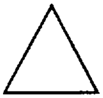
Abstract.— Hybrid HF-DFT calculations have been carried out on pairs of neutral molecules and their conjugated bases in order to determine their gas-phase acidities (ΔH values). Fifteen compounds have been calculated, both carbon acids (methane, ethane, ethene, ethyne, cyclopropane, cyclopropene, tetrahedrane, cubane, bicyclo[1.1.0]butane and bicyclo[1.1.1]pentane and reference compounds (hydrogen fluoride, hydrogen chloride, water, dihydrogen, hydrogen cyanide). The results are excellent and allow to discuss some topics like ring strain, carbon hybridization, aromaticity and topological analysis of the electron density. © 1997 Elsevier Science Ltd.

INTRODUCTION

The notion of carbon acidity has been one of the cornerstones for the establishment of a general theory of organic chemistry. In carbon acids **XH**, usually very weak acids, the loss of a proton from a carbon atom results in a carbanion $\mathbf{X^-}$. Thus the acidity of carbon acids and the stability of carbanions are two aspects of the same reality. The problem has been discussed thoroughly in several monographs.[1-5]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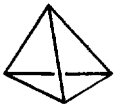
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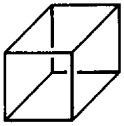
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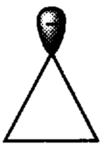
5


6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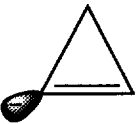
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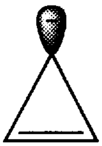
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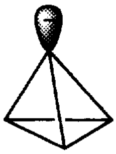
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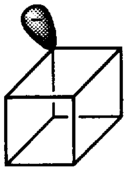
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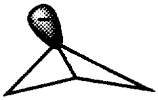
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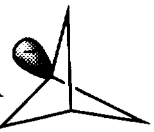

$\mathbf{6^-}$

In this paper, we will present a series of calculations of hydrocarbons (methane, ethane, ethene, ethyne, cyclopropane **1**, cyclopropene **2**, tetrahedrane **3**, cubane **4**, bicyclo[1.1.0]butane **5** and bicyclo[1.1.1]pentane **6**) and their corresponding carbanions using the hybrid HF-DFT approach (Becke3LYP/6-311++G**). For comparative purposes, some simple acids and their conjugated bases have also been calculated (hydrogen fluoride, hydrogen chloride, water, dihydrogen, hydrogen cyanide). Although the main purpose of this paper is to discuss gas phase carbon acidity and its relationship with ring strain, some other aspects like aromaticity, hybridisation, bond critical points will also be examined as well as the acidity of the above compounds in water (pK_a). We have previously described the heats of formation of azatetrahedranes[6] and azacubanes[7] as well as the basicity of tetrahedrane itself **3**.[8]

RESULTS AND DISCUSSION

We have reported in Table 1 the main results of our calculations, more details are given in the "Computational Details" section. The experimental gas-phase acidity values and pK_a values come from the references given in brackets.

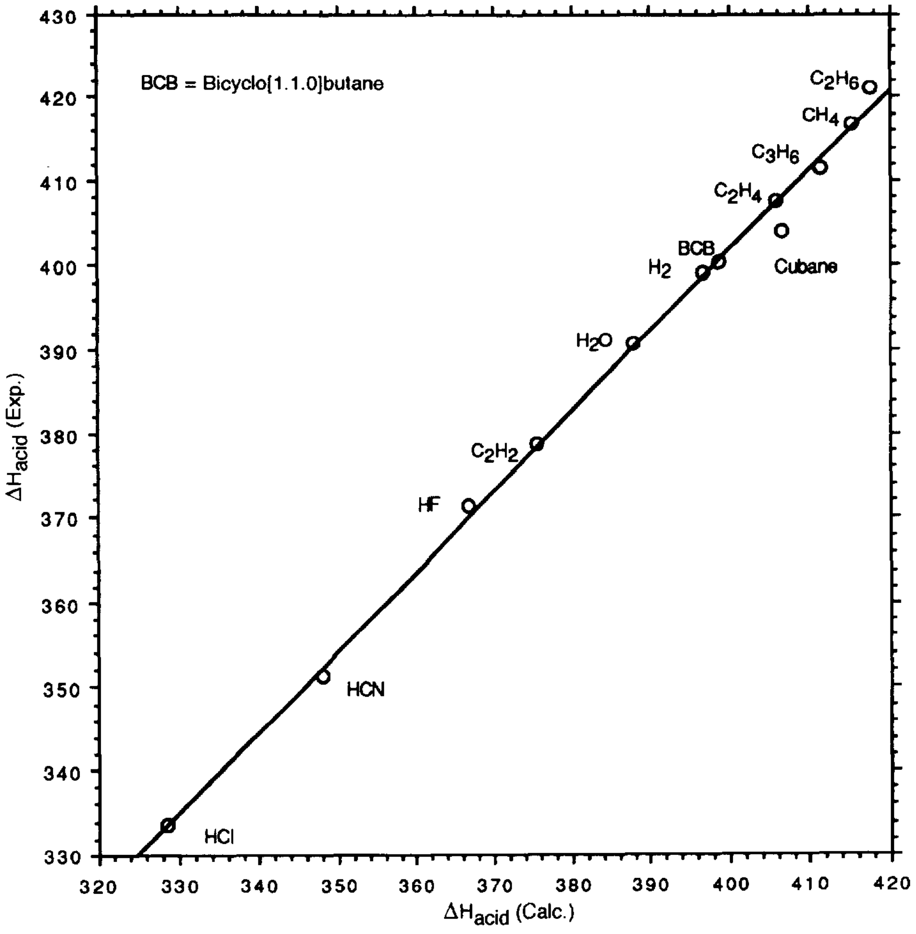
Table 1. Results of the Becke3LYP/6-311++G** calculations (1 hartree = 627.71 kcal mol^{-1})

Compound	**XH** total energy (hartrees)	**X$^-$** total energy (hartrees)	Calc. ΔH_{acid} (kcal mol^{-1})	Calc. ΔH_{acid} with ZPE (kcal/mol^{-1})	Exp. ΔH_{acid} (kcal mol^{-1})	pK_a
CH_4	-40.533957	-39.856210	425.29	415.21	416.6 [9]	48.0 [1]
C_2H_6	-79.856572	-79.174340	428.11	417.37	421.0 [9]	50.0 [1]
C_2H_4	-78.615538	-77.953388	415.51	405.81	407.5 [9]	44.0 [1]
C_2H_2	-77.356662	-76.745894	383.26	375.43	378.8 [9]	25.0 [1]
Cyclopropane	-117.930937	-117.258426	422.01	411.54	411.5 [9]	46.0 [1]
Cyclopropene[a]	-116.654350	-116.028141	392.95	384.02	------	29.0 [2][c]
Cyclopropene[b]	-116.654350	-115.970796	428.94	418.24	------	------
Tetrahedrane	-154.681139	-154.049889	396.12	387.33	------	------
Cubane	-309.532835	-308.868516	416.87	406.70	404.0 [10]	------
Bicyclo[1.1.0]butane	-155.991197	-155.343620	406.36	396.70	399.2 [9]	------
Bicyclo[1.1.1]pentane	-195.311370	-194.644642	418.38	407.66	------	------
HF	-100.482384	-99.888693	372.55	366.69	371.3 [9]	3.17 [1]
HCl	-460.834024	-460.303708	332.78	328.58	333.7 [9]	-7.0 [1]
H_2O	-76.458531	-75.827448	396.01	388.00	390.7 [9]	15.74 [1]
H_2	-1.179571	-0.534164	405.00	398.68	400.4 [9]	35.0 [1]
HCN	-93.454505	-92.888478	355.19	347.95	351.2 [9]	9.20 [1]

[a]Loss of a C(sp^2)-H (X = **2a**); [b]Loss of a C(sp^3)-H (X = **2b**); [c]Estimated for trimethylcyclopropene.

Gas-phase acidity

We have represented in Fig. 1 the plot corresponding to eq. (1).



$$\Delta H_{acid}(\text{Exp.}) = 21\pm7 + 0.95\pm0.02\ \Delta H_{acid}(\text{Calc.}),\ n = 12,\ r^2 = 0.996 \qquad (1)$$

According to eq. (1), the fitted value for cubane **4** is 408.1 kcal mol^{-1} which is close to the upper experimental value (404 ± 3 kcal mol^{-1}) and the predicted values for cyclopropene (olefin CH, **2a**, and aliphatic CH, **2b**), tetrahedrane **3** and bicyclo[1.1.1]pentane **6**, are 386.5, 419.1, 389.6 and 409.0 kcal mol^{-1}. Thus, tetrahedrane, a compound never isolated, is predicted to be a compound as acid as water and to yield a stable anion.

Aqueous acidity

The pK_a values of Table 1 are only roughly related to gas phase values (either experimental or calculated). If only carbon acids are considered (ethane, methane, cyclopropane, ethene, ethyne, hydrogen cyanide) the correlations become excellent:

$$pK_a = -202\pm6 + 0.60\pm0.01\ \Delta H_{acid}(\mathrm{Exp.}),\ n = 6,\ r^2 = 0.998 \qquad (2)$$

$$pK_a = -196\pm5 + 0.59\pm0.01\ \Delta H_{acid}(\mathrm{Calc.}),\ n = 7,\ r^2 = 0.998 \qquad (3)$$

These equations predict for cubane **4** a pK_a = 40.8 (Eq. 2) and 43.4 (Eq. 3) and for bicyclo[1.1.0]butane **5** a pK_a = 37.9 (Eq. 2) and 37.5 (Eq. 3). Eq. (3) predicts for bicyclo[1.1.1]pentane **6** a pK_a = 44.0 and for the CH_2 of cyclopropene a pK_a = 50.2 (anion **2b**$^-$).

Acidity, carbon hybridization and density at the bond critical points

It is known from old[2] that there is a linear relationship between acidity and the percentage of *s* character of the carbon atom. For six compounds, ethane (25 %),[2] cubane (31 %),[11] cyclopropane (30 %),[2] ethene (33 %),[2] cyclopropene (44 %)[2] and ethyne (50 %), [2] there is a good relationship:

$$\Delta H_{acid}(\mathrm{Calc.}) = 462\pm3 - 1.74\pm0.07\ (\%\ \text{of } s\text{-character}),\ n = 6,\ r^2 = 0.993 \qquad (4)$$

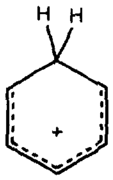
Another similar equation relates the acidity to the angle X-C-X of the carbon atom bearing the H atom of methane (109.47°), cubane (90°) and tetrahedrane (60°):

$$\Delta H_{acid}(\mathrm{Calc.}) = 354\pm5 + 0.57\pm0.06\ (\text{X-C-X angle in } ^\circ),\ n = 3,\ r^2 = 0.990 \qquad (5)$$

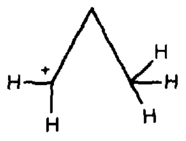
The ring strain decreases the *s*-character and increases the acidity.

Aromaticity

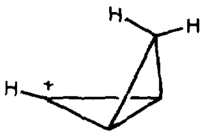
Four hydrocarbons belonging to this study are, in some ways, related to aromaticity: cyclopropane **1**,[12-14] cyclopropene **2**,[12,15,16] tetrahedrane **3**[12] and cubane **4**.[17,18] In the case of hydrocarbons, there is a direct relationship between aromaticity and basicity since protonation destroys aromaticity.



$C_6H_7^+$



1H$^+$



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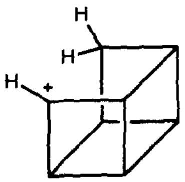


4H$^+$

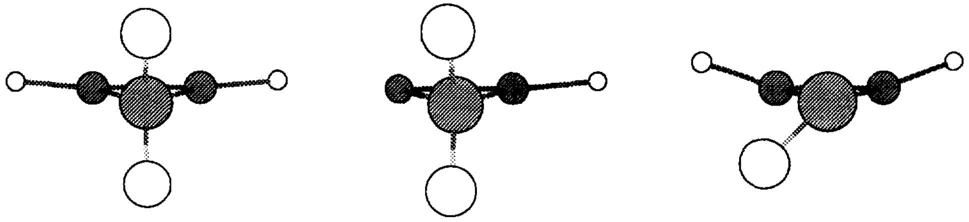
Protonation of benzene leads to the non-aromatic phenonium ion, $C_6H_7^+$,[1] while protonation of cyclopropane is accompanied by ring opening and formation of **1H**$^+$.[1] We have explained the high basicity of tetrahedrane by the releasing of strain energy in the open protonated form, **3H**$^+$.[8] Finally, cubane protonation also results in an opening of the structure, **4H**$^+$.[17,18]

On the other side, deprotonation preserves aromaticity: benzene, cyclopropane, tetrahedrane and cubane anions have the same electronic structure as their precursors. The Atoms in Molecules (AIM)[19] analysis of compounds **1**, **3** and **4** and their anions (see next section) show these similarities. Nevertheless, the fact that benzene (ΔH_{acid} = 400.7 kcal mol^{-1})[9] is more acid than ethene (407.5 kcal mol^{-1}, Table 1) is indicative of some influence of aromaticity on the acidity of hydrocarbons.

The case of cyclopropene should be discussed separately. The two anions **2a**$^-$ and **2b**$^-$ (Fig. 2) are very different. The most stable is the anion resulting from losing a proton from the olefin carbons, **2a**$^-$. Due to steric strain, there is considerable increase of the acidity from ethene to cyclopropene. The other anion, **2b**$^-$, is much less stable, 34.22 kcal mol^{-1} less; part is due to changes in the *s*-character (between ethane and ethene there is 11.56 kcal mol^{-1} of difference in acidity), but part is due to the fact that anion **2b**$^-$ is antiaromatic, or, at least, would be antiaromatic if planar, since the ring strain is larger in cyclopropene (X-C-X angle = 50.6°) than in cyclopropane (X-C-X angle = 60°) while the first is less acidic (418.24 kcal mol^{-1}) than the second (411.54 kcal mol^{-1}). The difference in stability between **2a**$^-$ and **2b**$^-$ is also reflected in the corresponding pK_a's: 29.0 and 50.2, near 20 pK_a units. Breslow reported in 1974 that the pK_a of compound 1,2,3-triphenylcyclopropene, a trisubstituted derivative of **2** without olefin protons, to be 50 (the effect of the three phenyl rings is difficult to be estimated).[16]

Geometries and AIM Analyses

Small geometric differences are observed between the neutral molecules and the corresponding anions since in most of the studied cases the substitution of the hydrogen (neutral molecules) by the lone pair (anions) does not change the electronic structure of the molecules. The only exception is the pyramidal carbanion **2b**$^-$ as can be seen in Fig. 2.



2 **2a**$^-$ **2b**$^-$

Fig. 2

The AIM analysis[19] shows a high electron density in the center of the rings for those compounds with three membered rings (**1**, **2**, **3**, **5**) and much lower in those formed by four membered rings (**4** and **6**). These results are in agreement with previous reports that indicate the possibility of aromaticity in thre membered rings but not in four membered ones.[12]

Table 1. Electronic density (ρ) at the critical points located in the center of the folowing cyclic systems (B3LYP/6-311++G**)

	ρ	ρ anion
C_3H_6 **1** → **1**$^-$	0.19352	0.18637
C_3H_4 **2** → **2a**$^-$	0.20963	not found
C_3H_4 (antiaromatic) **2** → **2b**$^-$	0.20963	0.18433
Tetrahedrane **3** → **3**$^-$	0.17871 0.19279*	0.17157 0.17872*
Cubane **4** → **4**$^-$	0.03109 0.08045*	0.03274 0.07997
Bicyclo[1.1.0]butane **5** → **5**$^-$	0.19862*	0.1857*
Bicyclo[1.1.1]pentane **6** → **6**$^-$	0.09897	0.09328

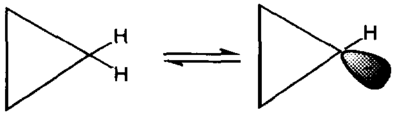
* Ring critical point of one of the three/four-membered rings (faces of the polyhedra)

Only a poor correlation between the ρ value at the C-H bond critical points that is broken in the processes studied here and the calculated ΔH_{acid} is found (Eq. 6).

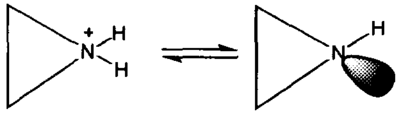
$$\Delta H_{acid} = 1165 \pm 180 - 2742 \pm 648\ \rho,\ n = 11,\ r^2 = 0.67 \qquad (6)$$

Conclusions

The computational results presented in this paper demonstrate that DFT calculations at the B3LYP/6-311++G** level are able to predict C-H acidities and probably N^+-H acidities (amine basicities, for instance, aziridine **7**) as well. Two recent publications show that this approach yields heats of formation of hydrocarbons[20] and C-H bond dissociation energies[21] well within the current experimental error limits.



1 **1**$^-$



7H$^+$ **7**

COMPUTATIONAL DETAILS

Calculations have been performed with the Gaussian 94 program[22] using the 6-311++G** basis set[23] at the hybrid HF-DFT, B3LYP, level of theory.[24] All the structures have been fully optimized using the EF minimization algorithm and the PRECISE keyword. The minimum nature of the structures obtained have been confirmed by analyzing the force constant matrix.

Supplementary material

All geometries are available on simple request to one of us (I. A.).

Acknowledgements

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