Acidity of hydrofullerenes: a quantum chemical study

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Guided by the idea that the acidity of hydrofullerenes might decrease with increasing level of hydrogenation and the possibility of using a pH-dependent regime to separate the various hydrogenated species (as predicted by Taylor and Walton), a theoretical pK_a scale for a series of hydrofullerenes has been set up.

Owing to the lack of experimental data on the acidity of most of these hydrofullerenes, this acidity scale has been established *via* test compounds using a correlation of experimental pK_a values in DMSO with calculated deprotonation energy values ΔE in the gas phase.

Besides the deprotonation energy, ΔE, the charge on the acidic hydrogen, the molecular electrostatic potential (MEP) and the electronic delocalization Δ are also calculated at the 3-21G level for the test compounds as well as for the hydrofullerenes, for interpretational purposes.

The interpretation of the calculated acidity sequence shows that besides a localized effect such as charge on the acidic proton (and the MEP in its neighbourhood), the electronic delocalization in the conjugate base, quantified *via* a Mulliken population analysis, is also highly important.

The dual correlation between the experimental pK_a values and the q_H and Δ values shows that the delocalization term accounts for about 75% of the calculated acidity.

The calculated acidity sequences are in agreement with the Taylor and Walton prediction pointing out an acidity decrease with increasing number of hydrogen atoms.

For a given q_H, the acidity is lower than in the model systems, indicating that the delocalization effects are of special importance in the hydrofullerenes. The calculation of the Δ quantity indeed shows a high electronic delocalization of the conjugate bases of the hydrofullerenes, which is almost the same (≈ 1 electron) throughout the series considered. The calculations on the global softness of the hydrofullerenes and their conjugate bases using Koopmans' theorem show a decrease with increasing number of hydrogens in both cases. In general all tendencies obtained indicate that the cage as a whole influences the acidity of the hydrofullerenes.

Introduction

The production of preparatively useful quantities of fullerenes[1] and the preparation of functional derivatives of these carbon clusters have continued in recent years to stimulate much experimental and theoretical research on the often unique properties of these materials.[2-5]

Among a variety of addition reactions,[6-9] the hydrogenation of the fullerenes C_{60} and C_{70} has been performed by practically all current reducing methods. Recent papers have reported the monitoring of addition reactions, including hydrogenation, by HPLC[10,11] while the assignment of the hydrogen contents of the generated stable caged hydrocarbons, called hydrofullerenes, has until now relied on mass spectral data.[12,13] $C_{60}H_2$ and $C_{70}H_2$ appear to result from hydroboration,[14,15] hydrozirconation[16] and other chemical reductions (with diimide,[17] with chromium(II) salts[17] and with zinc–acid,[18] whereas high hydrogen levels such as in $C_{60}H_{36}$ and $C_{70}H_{36}$ (with $C_{60}H_{18}$, $C_{60}H_{24}$ and $C_{60}H_{44}$ as minor products) are obtained mainly by Birch reduction,[19,20] but also by hydrogen atom transfer,[21] hydrogen radical induced hydrogenation[22] and by catalytic and solid phase hydrogenations.[17,23,24]

The high number of possible regioisomers for each of these hydrofullerenes (*e.g.* 23 for $C_{60}H_2$, 143 for $C_{70}H_2$) explains the quantity of theoretical studies devoted to the stability, molecular geometry, electronic structure and energy of isomeric C_{60} and C_{70} hydrogenated species.[25-39] The local density functional method and the use of empirical hydrocarbon potentials allowed the determination of the geometry and electronic structure of $C_{60}H_{36}$ and $C_{60}H_{60}$.[25] The energies of all isomeric $C_{60}H_{12n}$ (n = 1–5) molecules with T_h symmetry have been calculated and revealed the higher thermodynamic stability of $C_{60}H_{36}$ and $C_{60}H_{48}$.[30,37,39] The energies of the possible $C_{60}H_2$ and $C_{70}H_2$ isomers have been calculated at the semi-empirical PM3† and *ab initio* Hartree–Fock level. Thirty hydrogenated fullerenes $C_{60}H_{2n}$ (n = 1–30) of which $C_{60}H_{36}$ showed the lowest strain, have been analysed by molecular mechanics (MM2/P2) and the PM3 methods.[33] MNDO,† AM1† and PM3 methods led to equilibrium geometries and vibrational spectra of various isomers of $C_{60}H_2$, $C_{60}H_{36}$ and $C_{60}H_{60}$.[31] $C_{60}H_{36}$ is predicted to have T symmetry with four unsaturated, benzenoid rings[35] and MNDO and AM1 calculations also showed the lowest heat of formation for the same isomer of $C_{60}H_{36}$.[34] The isomerism of $C_{60}H_{36}$ and $C_{70}H_{36}$ has been studied by MM,† Hartree–Fock (HF) and density functional theory (DFT).[38,40]

From hydrofullerene isomer stabilities it was possible to deduce the most probable hydrogen addition pattern (*vide infra*).[26-29] Note that these conclusions give a general picture of the modes of addition to the fullerene surface which are in perfect agreement with experimental data.[41,42]

In relation to the possible chemical behaviour, a prediction by Taylor and Walton[6] is worth noting; they state that hydrofullerenes might be highly acidic, but that this acidity should decrease with an increasing level of hydrogenation, so that it might be possible to use a pH-dependent regime to separate the various hydrogenated species.

In this paper, we report a theoretical approach to predict the

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† Acronym explanations: PM3, parametric method 3; MNDO, modified neglect of differential overlap; AM1, Austin model 1; MM, molecular mechanics.

acidity of a series of hydrofullerenes, most of them having received less or no attention in the above mentioned theoretical studies as far as their acidity is concerned. Starting from known acidities of a series of small organic compounds, an acidity scale is established for the hydrofullerenes and the various factors influencing the acidity sequences are analysed.

After optimization at the AM1[43] semi-empirical level, stable structures of $C_{60}H_2$ up to $C_{60}H_{12}$ and $C_{70}H_2$ are derived from the energetically favoured 1,2-addition pattern at the 6:6 interpentagonal bond (*i.e.* the fusion of two six-atom rings) of one or more of the six pyracylene units composing fullerene C_{60},[32,36,44] while the stable $C_{60}H_{24}$ results from 1,4-addition to six-atom rings. The structure of $C_{60}H_{36}$ results from a combination of these two addition patterns, with six hydrogens added to each pyracylene unit of the hydrofullerene.[35]

In the first step, we built an acidity scale in which the hydrofullerenes under consideration would fit, making use of a variety of substances as test compounds, *e.g.* carboxylic acids, hydrocarbons and water, which have known pK_a values, varying from 3.45 to 40 in DMSO at 25 °C.[45]

Actually the only experimental acidity values available for hydrofullerenes are data in DMSO at 25 °C, for $C_{60}H_2$ (pK_{a_1} = 4.7, pK_{a_2} = 16.5[46]) and for $C_{60}HBu^t$ (pK_a = 5.7[47]), both systems belonging to the most acidic hydrocarbons known up to now. A correlation is therefore set up between *ab initio* Hartree–Fock calculated deprotonation energies and pK_a values in DMSO at 25 °C, and later is applied to the hydrofullerenes. The theoretically obtained acidity sequences for the test compounds and the hydrofullerenes are interpreted *via* traditional quantum chemical reactivity descriptors,[48] such as the Mulliken charge (q_H) on the acidic hydrogen and the molecular electrostatic potential (MEP) at a fixed distance r from the proton, and combined with a DFT based descriptor namely the global hardness of the systems considered.

In analogy to our approach in previous acidity and basicity studies on various organic and inorganic systems,[49–56] all of these descriptors were used to investigate effects that can influence a compound's acidity *e.g.* the inductive effect and the electronic delocalization effect.

Theory and computational details

The hydrofullerenes selected for establishing the acidity scale were $C_{60}HBu^t$, $C_{60}H_2$, $C_{60}H_4$, $C_{60}H_6$, $C_{60}H_8$, $C_{60}H_{10}$, $C_{60}H_{12}$, $C_{60}H_{24}$, $C_{60}H_{36}$ and $C_{70}H_2$. For each test compound and each hydrofullerence we calculated the deprotonation energy ΔE. The deprotonation energy of a compound, considered in our previous studies[54] as a measure of the pK_a, is defined in eqn. (1) where $E(AH)$ and $E(A^-)$ are respectively the

$$\Delta E = E(A^-) - E(AH) \qquad (1)$$

total energy for the acidic form of this compound and that of its conjugate base.

For a given value of n, the most stable $C_{60}H_{2n}$ isomer was considered and among its non-equivalent hydrogens we selected the most acidic one, *i.e.* the one with the lowest deprotonation energy. Intramolecular, as well as intermolecular, acidity sequences of our hydrofullerene series were obtained and using the regression equation ($pK_a = a\Delta E + b$) of the acidity scale for the test compounds, it was possible to attribute a pK_a value related to the ionization of the most acidic protons of these hydrofullerenes.

For each molecule of the test compounds and its conjugate base (*vide infra*) all structures were optimized, starting from the conformations showing the lowest energy using standard geometries[57] at the Hartree–Fock level with the 3-21G basis set.‡ The structures of the considered hydrofullerenes were constructed starting from the C_{60}[58] and C_{70} structures[59] with hydrogen atoms attached according to the literature data;[3,11,14,60–62] these structures were optimized at the semi-empirical level using the AM1 method. Starting from these equilibrium structures (test compounds and hydrofullerenes), all molecular properties such as the energies of the acidic systems and their conjugate bases, Mulliken populations, charges and electrostatic potentials were calculated at an *ab initio* level using the 3-21G basis set.

In the case of the hydrofullerenes, the conjugate bases resulting from abstraction of various types of hydrogen atoms were optimized at the AM1 level and a single point calculation at the 3-21G level was performed at the AM1 optimized structure leading to a set of deprotonation energies, (ΔE), from which the most acidic proton was selected. The intermolecular acidity sequence was then constructed with these ΔE values for the most acidic protons. Moreover two traditional quantum chemical properties, which can be expected to be related to the reactivity of the acids,[50–52,54–56] were calculated: the charge on the acidic proton and the molecular electrostatic potential (MEP) in its neighbourhood.

The charge on an atom k is calculated by subtracting the Mulliken population N_k[63] from its nuclear charge Z_k. The molecular electrostatic potential $V(R)$,[64] which expresses the interaction energy between the charge distribution of a molecule and a unit positive charge at a position R, is calculated from the electron density $\rho(r)$ and the nuclear charges Z_k (at positions R_k) eqn. (2). The MEP value is calculated at a

$$V(R) = \sum_k \frac{Z_k}{|R_k - R|} - \int \frac{\rho(r)}{|r - R|}\,dr \qquad (2)$$

chemically relevant distance of 4 au,§ as frequently used in our previous studies.[44,51,65] It was recognized that 4 au is the distance which a nucleophile can approach the target molecule without disturbing it in a significant way.[66]

A quantity describing electronic delocalization, Δ, was introduced for these systems; we propose to express it in terms of the amount of electrons leaving the C atom (which carries the acidic proton) upon deprotonation of the acid. The quantity defined here is then given by eqn. (3) where $N_C(n)$, $N_H(n)$ and

$$\Delta = [N_C(n) + N_H(n)] - N_C(n - 1) \qquad (3)$$

$N_C(n - 1)$ are the Mulliken populations at the C and H atoms of the acidic system and at the atom k of its conjugate base, respectively.

Finally the global hardness was considered to be a quantity of interest for the discussion. This quantity[67] is defined in eqn. (4)

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)} \qquad (4)$$

with E the energy and N the number of electrons in the system considered, this derivative being taken at a constant external potential $v(r)$. In a finite difference approximation using integer values for N, this expression can be rewritten as eqn. (5) where

$$\eta = \frac{E_i - E_{ea}}{2} \qquad (5)$$

E_i is the ionization energy and E_{ea} is the electron affinity.

Owing to the degeneracy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital

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‡ Cartesian coordinates of the optimized structures are available upon request from the authors.

§ 1 au ≡ $a_0 = 5.292 \times 10^{-11}$ m.

Table 1 Experimental pK_a, deprotonation energy ΔE calculated from the energies of the acidic and basic forms (E_A, E_B), q_H and MEP for the acidic hydrogen (see text) for the test compounds. All values are given in au[a]

Acid	pK_a	E_A	E_B	ΔE	q_H	MEP
1 CF_3COOH	3.45	−521.495 663	−520.944 126	0.5515	0.4405	0.041 86
2 $CHCl_2COOH$	6.4	−1139.938 186	−1139.385 263	0.5529	0.4346	0.036 64
3 PhCOOH	11.0	−415.990 384	−415.406 706	0.5837	0.4176	0.024 20
4 CH_3COOH	12.3	−226.534 236	−225.933 097	0.6011	0.4103	0.024 09
5 Cyclopentadiene	18.0	−191.717 080	−191.109 423	0.6077	0.2424	0.005 23
6 Indene	20.1	−343.535 284	−342.928 694	0.6066	0.2455	0.006 12
7 PhC≡CH	28.7	−304.672 958	−304.044 544	0.6284	0.3444	0.015 90
8 H_2O	31.2	−75.585 959	−74.868 630	0.7173	0.3666	0.025 39
9 NH_3	41	−55.872 203	−55.135 993	0.7362	0.2919	0.013 18
10 $PhCH_3$	43	−268.240 220	−267.553 671	0.6865	0.2377	0.007 89
11 CH_2=$CHCH_3$	44	−116.424 008	−115.723 574	0.7004	0.2198	0.006 21
12 CH_4	56	−39.976 878	−39.224 815	0.7521	0.1985	0.002 84

[a] Atomic units: $E = 4.360 \times 10^{-18}$ J, $q = 1.602 \times 10^{-19}$ C.

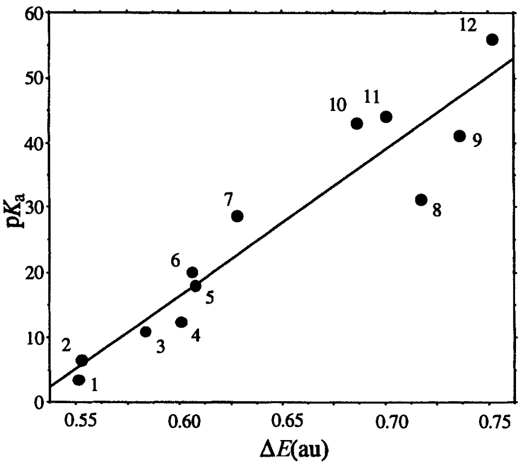


Fig. 1 pK_a *versus* ΔE for the test systems (numbering refers to Table 1)

(LUMO) of some hydrofullerenes, the calculations involving hydrofullerene cations and anions in eqn. (5) will be complicated by a Jahn–Teller distortion,[68] conflicting with the demand of the constant external potential in eqn. (4). Thus it was chosen to approximate E_i and E_{ea} by the energy of HOMO, ε_{HOMO}, and the energy of the LUMO, ε_{LUMO}, according to Koopmans' theorem.[69] This approximation leads to the current working equation for the global hardness [eqn. (6)]. The global softness is defined by eqn. (7).

$$\eta = \frac{\varepsilon_{LUMO} - \varepsilon_{HOMO}}{2} \quad (6)$$

$$S = \frac{1}{2\eta} \quad (7)$$

All calculations were performed with the GAMESS,[70] GAUSSIAN92[71] and GAUSSIAN94[72] programs on the CRAY Y-MP/116 computer of the Free Universities of Brussels combined with the UniChem software package[73] on a Silicon Graphics ONYX Extreme workstation.

Results and discussion

Test compounds

The 3-21G calculated energy of both acidic and basic forms and the deprotonation energy (ΔE) for the test compounds, are given in Table 1, together with the experimental pK_a values in DMSO, the values of the charge on the acidic hydrogen (q_H) and the molecular electrostatic potential (MEP) at a distance of 4 au from this acidic hydrogen.

The acidity sequence given by the experimental pK_a values is $CF_3COOH > CHCl_2COOH > PhCOOH > CH_3COOH > C_5H_6$ (cyclopentadiene) $> C_9H_8$ (indene) $>$ PhC≡CH $> H_2O > NH_3 > PhCH_3 > CH_2{=}CHCH_3 > CH_4$ whereas for the ΔE sequence, we find $CF_3COOH > CHCl_2COOH > PhCOOH > CH_3COOH > C_9H_8$ (indene) $> C_5H_6$ (cyclopentadiene) $>$ PhC≡CH $> PhCH_3 > CH_2{=}CHCH_3 > H_2O > NH_3 > CH_4$.

We find that the acidity given by the experimental data (pK_a) and by the theoretical calculations (ΔE) show the same sequence, except for the following cases: C_5H_6 is more acidic than C_9H_8; H_2O and NH_3 are more acidic than $PhCH_3$ and $CH_2{=}CHCH_3$ in DMSO, whereas, in the gas phase, C_5H_6 becomes less acidic than C_9H_8, H_2O and NH_3 become less acidic than $PhCH_3$ and $CH_2{=}CHCH_3$. In the case of the C_5H_6 and C_9H_8 this inversion of the trend in acidity from solution (DMSO) to the gas phase has already been mentioned by Taft and Bordwell.[74] They found that this effect is due to DMSO solvation which stabilizes the conjugate base $C_5H_5^-$ better than $C_9H_7^-$ resulting in a higher acidity for C_5H_6 than for C_9H_8. In the case of H_2O, NH_3, $PhCH_3$ and $CH_2{=}CHCH_3$, the inversion of the trend in acidity in solution and in the gas phase can be assigned to the opposite electronic effect of alkyl groups, known as electron donors in solution and showing dual character in the gas phase. This duality in the character of alkyl groups is observed experimentally when comparing the gas phase[75] and solution[76] acidities of the alkyl alcohol compounds. In our previous work this effect was explained[52] on the basis of our calculated group electronegativities and hardnesses. These findings are easily observed in the other cases where alkyl groups were found to show electron withdrawing properties as in carbanion[77] and carboxylic systems.[51] In solution the donor character of the alkyl group[46] dominates, whereas in the gas phase both negative and positive charges can be stabilized by an alkyl group. This effect shows that the alkyl groups yield a higher acidity in the gas phase (the lower ΔE values corresponding to higher acidity) than in solution which explains the case of the $PhCH_3$ and $CH_2{=}CHCH_3$.

When the ΔE values calculated by the 3-21G method are correlated with the experimental pK_a data (see Fig. 1), a correlation coefficient $r^2 = 0.892$ is obtained. Selecting only the carbon acids, and now including also $C_{60}H_2$ in order to broaden the pK_a range, now extending from 4.7 to 56, a correlation coefficient (r^2) of 0.988 is obtained (see Fig. 2).

The regression equation corresponding to $r^2 = 0.988$ is given in eqn. (8). The acidity sequence given by ΔE can be interpreted

$$pK_a = 258.423\,\Delta E - 136.648 \quad (8)$$

using the two traditional reactivity descriptors, q_H and MEP. When correlating the q_H values (see Table 1) with solution acidity (pK_a values), Fig. 3 shows a poor correlation, with a correlation coefficient of only $r^2 = 0.630$ with cyclopentadiene

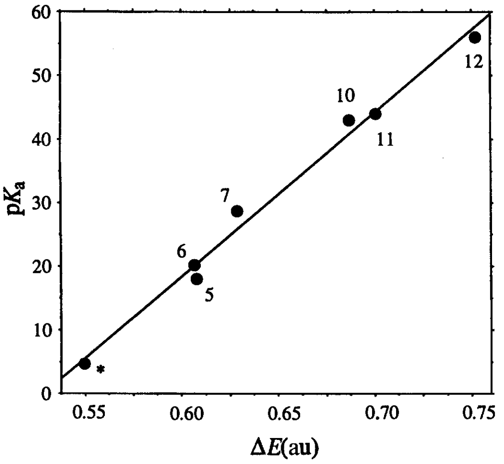


Fig. 2 pK_a *versus* ΔE for the carbon acids (numbering refers to Table 1; * refers to $C_{60}H_2$)

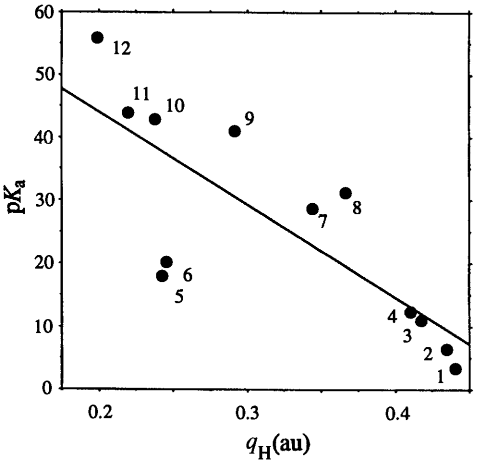


Fig. 3 pK_a *versus* q_H for the test systems (numbering refers to Table 1)

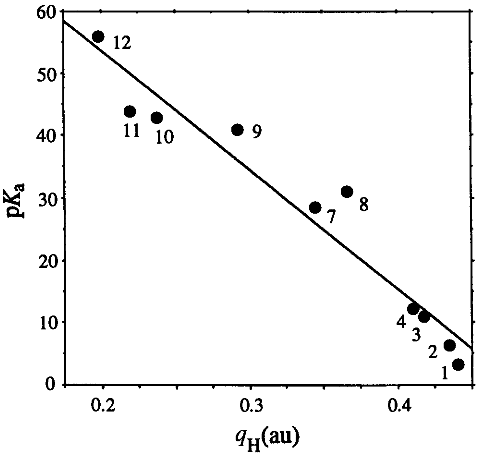


Fig. 4 pK_a *versus* q_H without cyclopentadiene and indene (numbering refers to Table 1)

and indene as outliers. If we repeat the same correlation without the values for cyclopentadiene and indene, this correlation coefficient is highly improved, up to $r^2 = 0.936$ (Fig. 4), this value further increasing to $r^2 = 0.938$ when PhC≡CH is removed.

In order to explain this problem, we have considered the reactivity sequence given by q_H which is $CF_3COOH > CHCl_2COOH > PhCOOH > CH_3COOH > H_2O > PhC{\equiv}CH > NH_3 > C_9H_8 > C_5H_6 > PhCH_3 > CH_2{=}CHCH_3 > CH_4$. This reactivity sequence shows that C_9H_8 and C_5H_6 are much less acidic in comparison with the solution

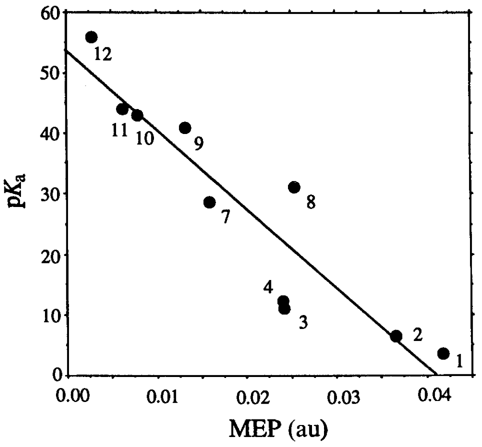


Fig. 5 pK_a *versus* MEP for the test systems without cyclopentadiene and indene (numbering refers to Table 1)

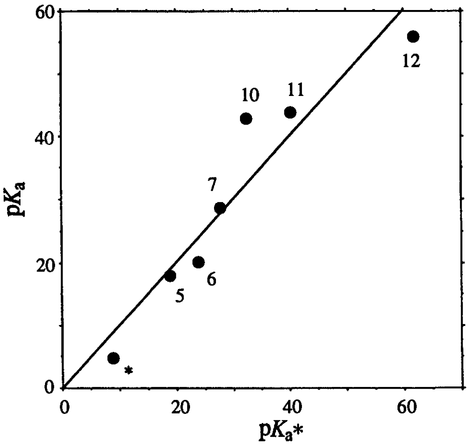


Fig. 6 Experimental pK_a *versus pK*$_a$ obtained *via* dual correlation [eqn. (9)] for the test systems (pK_a*). (Numbering refers to Table 1; * refers to $C_{60}H_2$); numerical data pK_a (pK_a*): $C_{60}H_2$ 4.7 (9.0); cyclopentadiene 18.0 (19.0); indene 20.1 (24.0); PhC≡CH 28.7 (27.8); $PhCH_3$ 43 (32.5); $CH_2{=}CHCH_3$ 44 (40.3); CH_4 56 (61.8).

(pK_a) acidity sequences (*vide infra*) and PhC≡CH becomes less acidic than H_2O.

By correlating pK_a and the MEP we found results comparable to the q_H case. The poor correlation coefficient gets better ($r^2 = 0.543 \rightarrow r^2 = 0.858$) when the cyclopentadiene and indene values are removed (only this case is shown, see Fig. 5), and is further improved ($r^2 = 0.865$) when PhC≡CH is removed.

These results can be interpreted by the fact that in the case of q_H and the MEP only the acidic form of the acid–base equilibrium system is considered, whereas in the case of the experimental pK_a and the theoretical ΔE both the acidic form and its conjugate base are involved. Our analysis predicts that these conjugate bases are highly stabilized by charge delocalization. This is confirmed by the delocalization quantity Δ calculated using eqn. (3) (see Table 2) showing higher values for cyclopentadiene and indene compared with PhC≡CH. The importance of delocalization effects upon the acidity of various compounds has already been recognized in the past.[78]

Finally, in order to underline the complementarity between q_H and Δ in the description of the acidity, we set up a dual correlation for the hydrocarbon compounds between the experimental pK_a values and the q_H and Δ values. This correlation (shown in Fig. 6) has a correlation coefficient $r^2 = 0.900$. The expression for this dual correlation is given in eqn. (9) and shows that upon increasing q_H and Δ, the acidity

$$\mathrm{p}K_a = -100.584\, q_H - 117.511\, \Delta + 154.678 \qquad (9)$$

increases (lower pK_a value). The pK_a values calculated by this equation are given in Fig. 6. Upon analysing the relative contributions of both terms we see that the delocalization term accounts for about 75% of the calculated acidity. The basic form is an important factor in the pK_a value. The charge on the most acidic hydrogen, a descriptor of the acidic form, together with the delocalization of the electrons referring to both acidic and basic form, yield a very good description of acidity.

Hydrofullerenes

In Table 3 we put together the symmetry of the most stable isomers of the hydrofullerenes used in the present study and the experimentally available pK_a values.

Table 2 Electronic delocalization Δ calculated from the Mulliken populations (N_C, N_H and N_{C^-}) (see text) for the hydrocarbon systems (all values in au[a])

Acid	N_C	N_H	N_{C^-}	Δ
$C_{60}H_2$	6.3113	0.7105	6.0300	0.9917
Cyclopentadiene	6.4922	0.7576	6.3025	0.9473
Indene	6.4605	0.7545	6.3142	0.9008
$PhC\equiv CH$	6.3638	0.6555	6.2346	0.7847
$PhCH_3$	6.2301	0.7623	6.1561	0.8363
$CH_2{=}CHCH_3$	6.2268	0.7802	6.2216	0.7854
CH_4	6.7939	0.8015	6.9759	0.6195

[a] Atomic unit = 1.602×10^{-19} C.

Table 3 Experimental pK_a values and symmetry of the hydrofullerenes considered

Hydrofullerene	Symmetry	Ref.	pK_a
C_{60}	I_h	58	
$C_{60}HBu^t$	Cs	3	5.74 (47)
$C_{60}H_2$	C_{2v}	60	4.7 (46)
$C_{60}H_4$	C_s	60	
$C_{60}H_6$	C_{3v}	60	
$C_{60}H_8$	C_s	60	
$C_{60}H_{10}$	C_{2v}	60	
$C_{60}H_{12}$	T_h	60	
$C_{60}H_{24}$	T_h	3	
$C_{60}H_{36}$	T_h	61	
C_{70}	D_{5h}	59	–
$C_{70}H_2$	C_s	14	> pK_a $C_{60}H_2$ (14,17)

The geometries obtained after AM1 optimization are shown in Fig. 7, the various hydrogen atom types are indicated and the most acidic hydrogens are denoted as Ha.

The most acidic hydrogen in each system was selected on the basis of the deprotonation energies (Table 4) which were calculated (3-21G) in an analogous way to the test systems, now for each hydrogen type in a given hydrofullerene. The deprotonation energy and the descriptors also used for the test systems are summarized in Table 5. On this basis the following intermolecular acidity sequence of the hydrofullerenes is obtained: $C_{60}H_2 > C_{60}H_4 > C_{60}H_6 > C_{60}H_8 > C_{60}H_{10} > C_{60}H_{12} > C_{60}H_{24} > C_{60}H_{36}$. This is in agreement with the Taylor and Walton prediction that the acidity would decrease with increasing hydrogen level.

This finding is interpreted both by the Mulliken charge, q_H, on the acidic hydrogen and by the MEP calculated at a distance of 4 au, from this acidic hydrogen along the C–H axis, both values leading to the same acidity sequences as ΔE (Table 5). If we take a closer look at the ΔE values for $C_{60}HBu^t$ and $C_{60}H_2$, we remark that $C_{60}HBu^t$ is more acidic than $C_{60}H_2$, whereas the experimental pK_a values show the inverse sequence. This problem is explained by the opposite effect of the alkyl group in the gas phase and in solution as previously described. The Bu^t group is an electron donor in solution while an electron attractor in the gas phase. Thus the acidity of the $C_{60}HBu^t$ increases in the gas phase.

When plotting the calculated pK_a value (p$K_{a,cal}$) *versus n* [Fig. 8(*a*)] the p$K_{a,cal}$ increases with *n*; it should be noted it increases

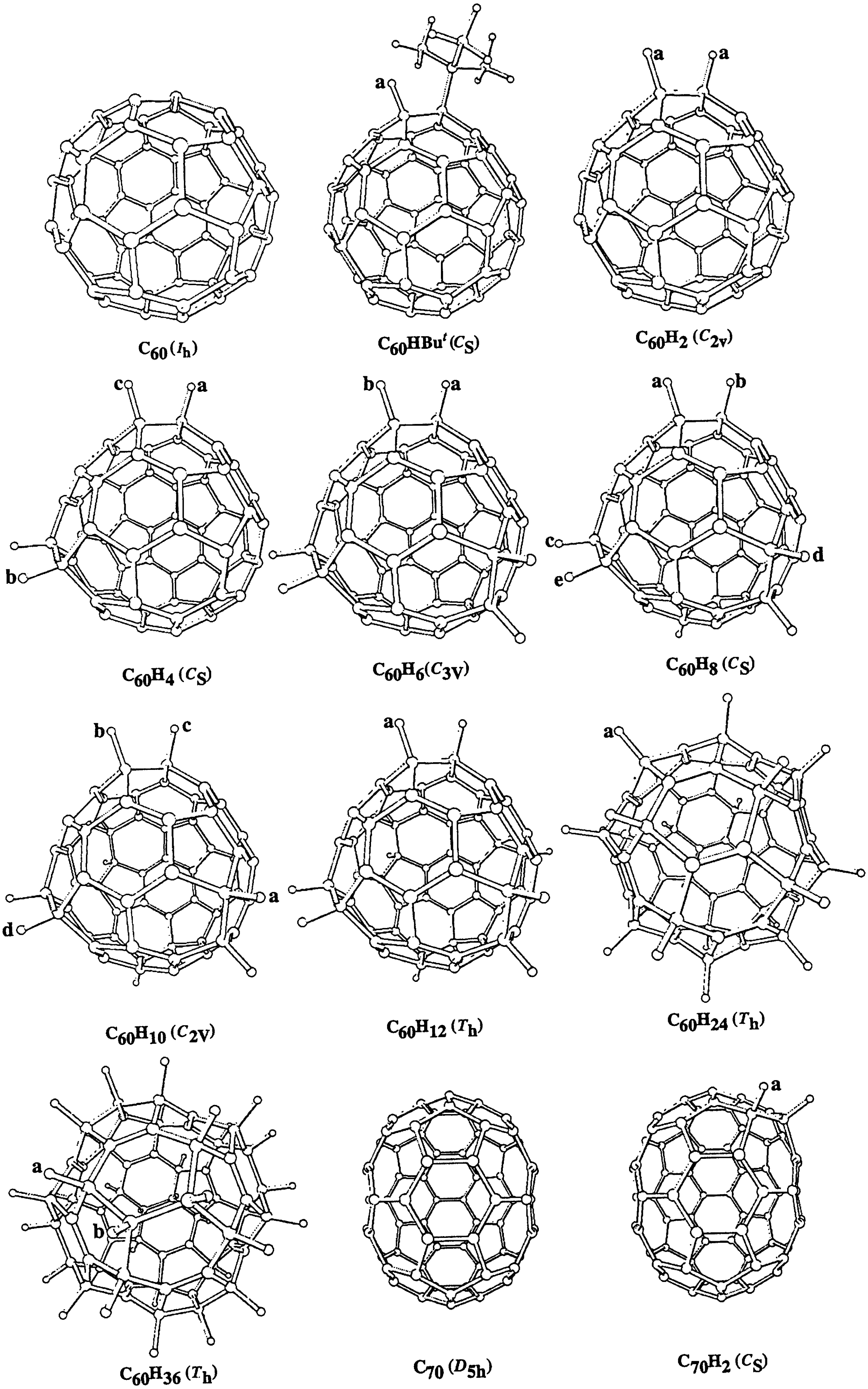
Table 5 Deprotonation energy ΔE, q_H and MEP (all values in au) and pK_a values calculated *via* regression eqn. (8) for the most acidic hydrogen in the hydrofullerene systems (*n* = number of hydrogens)

Hydrofullerene	*n*	ΔE	p$K_{a,cal}$	q_H	MEP[a]
1 $C_{60}HBu^t$	1	0.5415	3.31	0.2988	
2 $C_{60}H_2$	2	0.5498	5.45	0.2895	0.024 87
3 $C_{60}H_4$	4	0.5527	6.20	0.2873	0.022 18
4 $C_{60}H_6$	6	0.5600	8.09	0.2836	0.019 33
5 $C_{60}H_8$	8	0.5628	8.80	0.2797	0.016 79
6 $C_{60}H_{10}$	10	0.5648	9.32	0.2778	0.014 27
7 $C_{60}H_{12}$	12	0.5687	10.33	0.2744	0.011 88
8 $C_{60}H_{24}$	24	0.6294	26.01	0.2433	0.004 15
9 $C_{60}H_{36}$	36	0.6501	31.35	0.2240	0.001 91
10 $C_{70}H_2$	2	0.5385	2.53	0.2911	0.025 63

[a] Atomic unit, *cf.* Table 1.

Table 4 Deprotonation energy ΔE calculated from E_A and E_B (see Table 1) for each hydrogen type (see Table 4) in $C_{60}HBu^t$, $C_{60}H_2$, $C_{60}H_4$, $C_{60}H_6$, $C_{60}H_8$, $C_{60}H_{10}$, $C_{60}H_{12}$, $C_{60}H_{24}$, $C_{60}H_{36}$, and $C_{70}H_2$ (all values in au)

Hydrofullerene	Hydrogen type	E_A	E_B	ΔE
$C_{60}HBu^t$	a	−2415.473 890	−2414.932 396	0.541 49
$C_{60}H_2$	a	−2260.205 197	−2259.655 422	0.549 77
$C_{60}H_4$	a	−2261.376 840	−2260.824 172	0.552 67
	b		−2260.823 519	0.553 32
	c		−2260.823 132	0.553 71
$C_{60}H_6$	a	−2262.548 886	−2261.988 878	0.560 01
	b		−2261.988 226	0.560 66
$C_{60}H_8$	a	−2263.717 917	−2263.155 156	0.562 76
	b		−2263.155 140	0.562 78
	c		−2263.154 815	0.563 10
	d		−2263.154 274	0.563 64
	e		−2263.152 407	0.565 51
$C_{60}H_{10}$	a	−2264.886 516	−2264.321 739	0.564 78
	b		−2264.321 283	0.565 23
	c		−2264.319 558	0.566 96
	d		−2264.317 131	0.569 38
$C_{60}H_{12}$	a	−2266.054 113	−2265.485 447	0.568 67
$C_{60}H_{24}$	a	−2273.073 487	−2272.444 115	0.629 37
$C_{60}H_{36}$	a	−2280.126 401	−2279.476 340	0.650 06
	b		−2279.184 733	0.941 67
$C_{70}H_2$	a	−2636.789 896	−2636.251 420	0.538 48



$C_{60}\,(I_h)$ $C_{60}HBu^t\,(C_s)$ $C_{60}H_2\,(C_{2v})$

$C_{60}H_4\,(C_s)$ $C_{60}H_6(C_{3v})$ $C_{60}H_8\,(C_s)$

$C_{60}H_{10}\,(C_{2v})$ $C_{60}H_{12}\,(T_h)$ $C_{60}H_{24}\,(T_h)$

$C_{60}H_{36}\,(T_h)$ $C_{70}\,(D_{5h})$ $C_{70}H_2\,(C_s)$

Fig. 7 Hydrofullerene geometries obtained after AMI optimization

Table 6 Electronic delocalization Δ calculated from Mulliken populations (N_C, N_H and N_{C^-} for the hydrofullerenes (all values in au)

Hydrofullerene	N_C	N_H	N_{C^-}	Δ
$C_{60}HBu^t$	6.2978	0.7012	5.9803	1.0187
$C_{60}H_2$	6.3113	0.7105	6.0300	0.9917
$C_{60}H_4$	6.3123	0.7126	6.0275	0.9975
$C_{60}H_6$	6.3114	0.7164	6.0309	0.9970
$C_{60}H_8$	6.3112	0.7203	6.0336	0.9979
$C_{60}H_{10}$	6.3119	0.7222	6.0310	1.0031
$C_{60}H_{12}$	6.3117	0.7256	6.0300	1.0073
$C_{60}H_{24}$	6.4272	0.7567	6.1641	1.0198
$C_{60}H_{36}$	6.3480	0.7760	6.1132	1.0108
$C_{70}H_2$	6.3107	0.7089	6.0182	1.0014

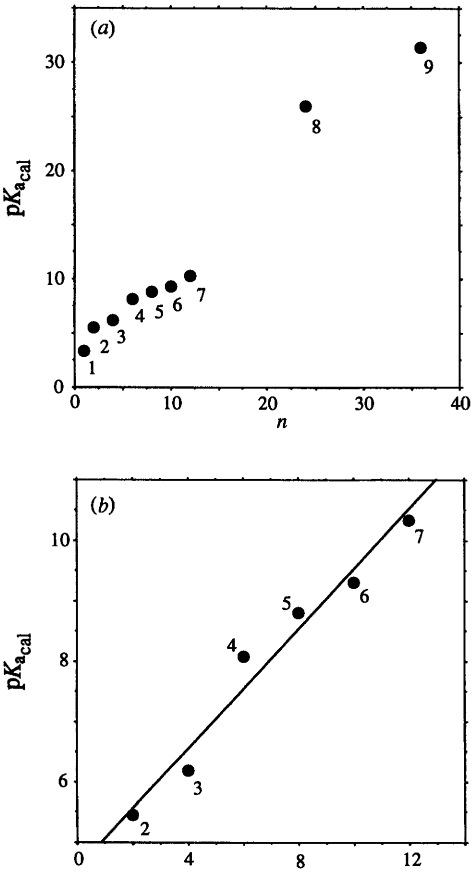


Fig. 8 (*a*) p$K_{a,cal}$ *versus n* for all hydrofullerenes; (*b*) without the $C_{60}H_{24}$ and $C_{60}H_{36}$ cases (numbering refers to Table 6)

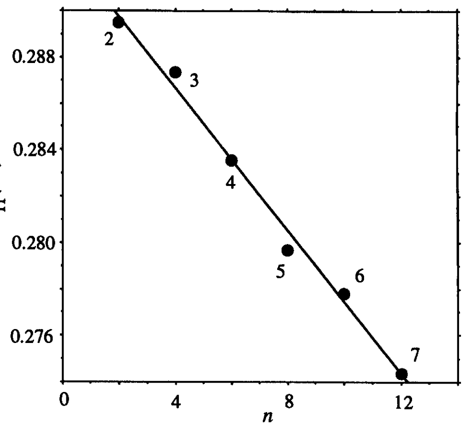


Fig. 9 q_H *versus n* for the hydrofullerenes (numbering refers to Table 6)

almost linearly with n for the series $C_{60}H_{2n}$, n = 1–6 [Fig. 8(*b*)]. This shows the influence of the whole of the fullerene cage on the acidity. In Fig. 8(*a*) we see that the values for $C_{60}H_{24}$ and $C_{60}H_{36}$ are situated above the regression line. For these higher hydrofullerenes, a lower acidity is expected, in accordance with the literature where a relatively high stability is attributed to these systems (and also to some other hydrofullerenes such as $C_{60}H_{60}$).[25,30,33,79]

This decreasing acidity sequence given by p$K_{a,cal}$ going from $C_{60}H_2$ to $C_{60}H_{36}$ is interpreted by the two quantum chemical descriptors, q_H and MEP. The charges q_H show, as in the case of p$K_{a_{cal}}$, a linear decrease with n (Fig. 9) with a correlation coefficient $r^2 = 0.992$. Similar behaviour is seen for the MEP (Table 5) where a correlation coefficient $r^2 = 0.999$ is found with n. Again these data indicate that the whole of the cage influences the acidity.

Although the regression equations pK_a *vs.* q_H are similar for the test systems and the hydrofullerenes, an important difference is that the pK_a value for a given q_H value is much higher in the case of the test compounds than in the case of the hydrofullerenes. For example in the case of the $CHCl_2COOH$, the pK_a equals 6.4 for a q_H value of 0.435, whereas in the case of the $C_{60}H_2$, pK_a = 4.7 for a q_H value of 0.289. A higher acidity is thereby found for $C_{60}H_2$ although the q_H is considerably smaller. The same tendency is observed in the case of the MEP. This aspect can be explained, as in the case of indene and cyclopentadiene, by the fact that the conjugate bases of the hydrofullerenes are stabilized by charge delocalization.

The calculation of the quantity Δ characterizing the charge delocalization given by eqn. (3) (see Table 6) shows for each hydrofullerene system an important delocalization, more or less constant in all systems considered. Approximately one electron delocalizes from the acidic site when passing from $C_{60}H_{2n}$ to $C_{60}H_{2n-1}^-$, the delocalization slightly increasing with the number of hydrogen atoms.

However, the increasing stability of the acidic systems[33] when going from $C_{60}H_2$ to $C_{60}H_{36}$ can explain the decreasing acidity in this direction. This stability of the acidic systems is due to the hydrogen additions which transform sp^2 carbon atoms into sp^3 carbon atoms (giving less strain in the cage);[33] a decrease in strain upon hydrogenation leads to a stability increase and less acidic character. In general in the case of the hydrofullerenes we can rely on the stability of the conjugate bases in order to explain the magnitude of this acidity and on the stability of the acid forms in order to explain the evolution of this acidity.

As an extension of our C_{60} based hydrofullerenes we also studied $C_{70}H_2$ which has already been investigated experimentally.[14,16] The analysis of the p$K_{a,cal}$ (see Tables 4 and 5) suggests that $C_{70}H_2$ is more acidic than $C_{60}H_2$. The interpretation of this result by the charges q_H and by MEP (Table 5), calculated in the same way as for $C_{60}H_2$, confirms this finding. These results however are not in agreement with literature data which predict that $C_{60}H_2$ is more acid than $C_{70}H_2$; this could be explained by a delocalization effect typical for the C_{70} structure not showing up in the comparison between $C_{60}H_2$ and $C_{70}H_2$. A precise experimental determination of the pK_a of $C_{70}H_2$ should be performed in order to settle this point. The actual estimate of the relative acidity is based on ^{1}H NMR shifts,[14,17] measuring only properties of the acidic form, whereas our calculations in Table 6 indicate a large value of the delocalization parameter for $C_{70}H_2$.

Finally, we tried to link the pK_a values obtained to the chemical hardness and softness of the systems considered and their conjugate bases. These values calculated using eqns. (6) and (7) are given, together with ε_{HOMO} and ε_{LUMO}, in Table 7. The values of global hardness, η, and global softness, S, for $C_{60}H_{2n}$ with n = 3, 6, 12 and 18 should be regarded as an approximation due to the degeneracy of the frontier orbitals.

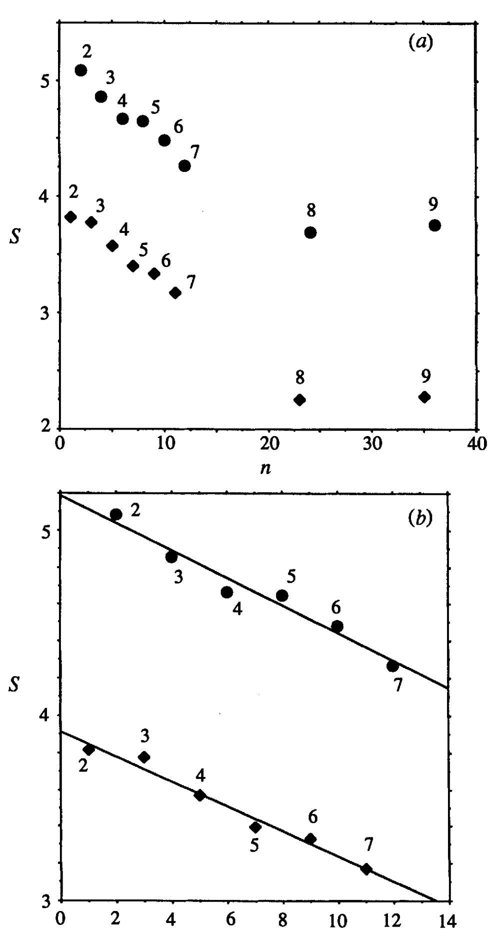


Fig. 10 (*a*) Total softness (in au) *versus* n for the hydrofullerenes (◆) and their conjugate bases (●); (*b*) total softness (in au) *versus* n for the hydrofullerenes (◆) and their conjugate bases (●) without $C_{60}H_{24}$ and $C_{60}H_{36}$ (numbering refers to Tables 6 and 9)

Table 7 Global hardness η and global softness S calculated from HOMO and LUMO energy values for the hydrofullerene systems[a] and their conjugate bases

Hydrofullerene	ε_{HOMO}	ε_{LUMO}	η	S
1 $C_{60}HBu^t$	−0.284 90	−0.022 01	0.1314	3.8039
2 $C_{60}H_2$	−0.286 18	−0.024 00	0.1311	3.8142
3 $C_{60}H_4$	−0.278 56	−0.013 75	0.1324	3.7763
4 $C_{60}H_6$	−0.287 79	−0.007 58	0.1401[a]	3.5687[a]
5 $C_{60}H_8$	−0.280 68	0.013 70	0.1472	3.3970
6 $C_{60}H_{10}$	−0.275 90	0.024 24	0.1501	3.3318
7 $C_{60}H_{12}$	−0.272 67	0.042 40	0.1575[a]	3.1739[a]
8 $C_{60}H_{24}$	−0.316 71	0.127 38	0.2220[a]	2.2518[a]
9 $C_{60}H_{36}$	−0.297 85	0.140 76	0.2193[a]	2.2799[a]
10 $C_{70}H_2$	−0.278 01	−0.028 29	0.1249	4.0045
Conjugate base				
1 $C_{60}Bu^{t-}$	−0.112 04	0.087 78	0.0999	5.0045
2 $C_{60}H^-$	−0.107 71	0.088 88	0.0983	5.0867
3 $C_{60}H_3^-$	−0.106 56	0.099 37	0.1030	4.8560
4 $C_{60}H_5^-$	−0.099 69	0.114 62	0.1072	4.6661
5 $C_{60}H_7^-$	−0.091 67	0.123 33	0.1075	4.6512
6 $C_{60}H_9^-$	−0.089 98	0.133 02	0.1115	4.4843
7 $C_{60}H_{11}^-$	−0.085 12	0.149 20	0.1172	4.2677
8 $C_{60}H_{23}^-$	−0.043 50	0.227 33	0.1354	3.6924
9 $C_{60}H_{35}^-$	−0.024 77	0.241 45	0.1331	3.7563
10 $C_{70}H^-$	−0.115 11	0.074 90	0.0950	5.2629

[a] Approximate values due to degeneracy of frontier orbitals in applying eqns. (6) and (7).

We see that for the series $C_{60}H_{2n}$ the softness decreases upon increasing n due to the presence of hard H atoms (η_H = 6.42 eV[80]) which will decrease the softness of the cage as a whole. The same tendency is observed in the case of the conjugate base $C_{60}H_{2n-1}^-$: the softness decreases upon increasing n, the value for a given n being always larger than that of the acid. When plotting both softnesses (of the acidic forms and their conjugate bases) as a function of n (Fig. 10) we see that either softness gives a good correlation with n up to n = 12 [Fig. 10(*b*)], except for $C_{60}H_{24}$ and $C_{60}H_{36}$ which deviate from the regression line shown in Fig. 8. This may be due to the geometric aspect (addition pattern) of these structures provoked by the larger number of hydrogen atoms and by their disposition on the pyracylenic units which is different from the cases of $C_{60}H_2$ to $C_{60}H_{12}$. The overall decrease in the softness of the conjugate base with increasing n indicates a less adequate stabilization of the conjugate base due to a decrease in charge capacity.[81] Again we see that the cage as a whole influences the acidity.

The correlation with acidity could further be interpreted using the hard and soft acids and bases (HSAB) principle[82] leading to a better interaction of the soft solvent DMSO with softer acids. DMSO can indeed be considered as a soft base. Comparing the η values for CO_2 (8.8 eV[81]) and SO_2 (5.6 eV[81]) we see that SO_2 is about one third softer than CO_2. The hardness of $(CH_3)_2CO$ is known to be equal to 5.6 eV, therefore by applying the same ratio, an approximate hardness value of 3.6 eV is given for DMSO, which indeed is very low.

Conclusions

The acidity scale established from the test compounds (3-21G calculated gas phase deprotonation energy *vs.* experimental pK_a values in DMSO at 25 °C) in order to investigate the acidity of the hydrofullerenes has permitted a discussion on the various factors influencing the acidity of these systems.

The interpretation of this acidity by traditional quantum chemical descriptors, such as the charge on the acidic proton and the MEP, suggests delocalization in the conjugate base to be an important factor influencing the acidity. The importance of this quantity is confirmed by a dual correlation between the experimental pK_a values and the q_H and Δ values.

The pK_a values calculated for the hydrofullerenes ($C_{60}H_{2n}$ with n = 1–6, 12 and 18 and $C_{70}H_2$) by the correlation equation for the model systems are in agreement with the experimental pK_a values (DMSO, 25 °C) available. The calculated acidity sequence is in agreement with the Taylor and Walton prediction pointing out an acidity decrease with increasing number of hydrogen atoms.

For a given value of q_H the acidity is lower than in the model systems, indicating that the delocalization effects are of special importance in the hydrofullerenes. The calculation of the Δ quantity indeed shows a high electronic delocalization of the conjugate bases of the hydrofullerenes, which is almost the same ($\approx$1 electron) throughout the series considered. The global softness calculated for the hydrofullerenes considered and their conjugate bases shows a decrease with increasing number of hydrogens, resulting in a less adequate stabilization of the conjugate base.

In general all tendencies show that the cage as a whole influences the acidity of the hydrofullerenes.

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