Charge delocalisation in hydrofullerenes and substituted hydrofullerenes: effect of deprotonation

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The delocalisation that occurs upon deprotonation of a series of hydrofullerenes and substituted hydrofullerenes is analysed. The charges and bond lengths of the acidic and basic forms of each system are considered. We find approximately one electron delocalising from the deprotonated C atom to the rest of the system on deprotonation. The softness of the cage and the bond alternation permit delocalisation of the resulting negative charge over the main part of the fullerene cage, following the pattern of conjugated bonds, showing a clear 'delocalisation path'. The same paths were found for hydrofullerenes and substituted hydrofullerenes, so that the properties of different functional groups are seen not to influence the delocalisation pattern in a significant way. This delocalisation greatly stabilises the basic form and explains the high acidities of these hydrocarbon systems.

The deprotonation energies for the two most stable $C_{60}H_2$ and the two most stable $C_{70}H_2$ isomers have been calculated at the *ab initio* HF/6-31G* level of theory. 5,6-$C_{70}H_2$ was found to be more acidic than 1,2-$C_{60}H_2$. This inversion as compared to ^{1}H NMR predictions results from the difference in cage structure of C_{60} and C_{70}. The delocalising charge reaches the equatorial band of six rings present in the C_{70} structure, giving rise to a better stabilisation of the basic form than for 1,2-$C_{70}H_2$.

Introduction

Since their discovery[1] and first macroscopic synthesis,[2] fullerenes have been the subject of much scientific research. One of the properties of the fullerenes that has caused some controversy over the years is the extent of aromaticity of these compounds and their derivatives. First predicted to be aromatic,[1] Buckminsterfullerene C_{60} soon appeared to be much less aromatic and hence more reactive than first assumed.[3] Failing to fit the predicted 'super-benzene' picture, a 'super-Kékulé-benzene' would probably have been a more correct definition of the system,[4] since there are two distinct and alternating bond lengths present in C_{60} (for more general reviews of the chemistry of the fullerenes, we refer to refs. 3, 5–9). Despite their extensive conjugation, the fullerenes behave as electron-poor alkenes.[10] Furthermore, the charges in the fullerenes are described as fairly localised, resulting in a higher reactivity than first predicted.[3] From this localized model, the aromaticity of the fullerenes is mostly seen as a local phenomenon.[3,11] However, the degree of aromaticity of the fullerenes and their derivatives is not totally clear. According to Taylor and Walton, owing to the poor electron delocalisation in the fullerenes, one may account for addition reactions in terms of localised structures, whereby adding electrons to the structure gives rise to aromaticity in certain pentagonal rings, and the driving force for octahedral addition to C_{60} is the creation of eight isolated benzenoid rings.[3] These benzenoid rings are also described for hydrogenated fullerenes of the type $C_{60}H_{60-6n}$ ($n = 1$–8), even with clear bond alternation present.[12] The chemistry of the fullerenes is suggested to proceed in such a manner that the reaction products become as aromatic as possible, resonance energy methods indicating that C_{60} is moderately aromatic with some olefinic character.[13] According to Haddon, the controversy in the description of the aromaticity of the fullerenes does not come from the fullerenes themselves, but from the lack of a reference system, and he thus proposes a rolled-up ball of graphite as reference system for describing the aromaticity of C_{60}, whereby the fullerenes are seen as a special class of strained and continuous aromatic compounds.[14]

In studying the acidity of fullerene derivatives, we have encountered another form of electron delocalisation that plays an important role in the reactivity of these systems. We found the electron delocalisation upon deprotonation of the acidic form to be a very important factor in the acidity of hydrogenated fullerenes.[15,16] This high delocalisation of charge is not in contradiction with the localised bonding in the acidic form. On the contrary, it further demonstrates the high conjugation from the alternation of single and double bonds and thus the conjugated alkene-like behaviour of these systems.[10]

The electron delocalisation upon deprotonation mainly results in significant stabilisation of the conjugate base. This high stabilisation is an important reason for the high acidity of these systems. Indeed, as the deprotonation is part of a simple acid–base equilibrium of the type $AH \rightleftharpoons A^- + H^+$, stabilisation of the basic form will favour the right-hand side of the equation. In order to quantify this electron delocalisation, we have introduced a parameter that determines the amount of charge that vanishes from the deprotonated C-atom to appear in the rest of the system. Calculation of this delocalisation or Δ-parameter shows a loss of about one electron for the deprotonated C-atom both for the hydrofullerenes and the substituted hydrofullerenes considered.[15,16] No prediction or estimation has, however, been made of the extent of this delocalisation, nor its relationship with the properties of the acidic and basic forms.

In order to establish the regions of the system into which this charge will be delocalised and how far over the system this delocalisation extends, we have set up a scheme for further analysis of this property. Geometries and charges of both acidic and basic forms of all systems considered were therefore plotted in order to follow the delocalisation and estimate its extent.

As an application of these ideas, the acidity of $C_{60}H_2$ and $C_{70}H_2$ is compared. Here the influence of the difference in cage structure on the delocalisation pattern and its extent, and hence the differential stabilisation of the respective conjugate bases will be analysed, concentrating on the interplay of electronegativity and charge capacity effects, as in our earlier studies of acidity and basicity in organic and inorganic systems,[17–24] including fullerenes.[15,16,25,26]

Theory and computational details

Two series of systems are considered in this study. The first is a series of hydrogenated fullerenes of the type $C_{60}H_{2n}$ with n = 1–6. These hydrofullerenes are derived from an 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 [60]fullerene.[15] As considered in our previous study, the basic form for each hydrofullerene was formed by removal of one H-atom, which gives rise to the lowest deprotonation energy if more than one type is present.[15]

A second series is derived from 1,2-$C_{60}H_2$ by substituting one H-atom with a functional group. The 1,2-C_{60}HR substituted hydrofullerenes considered are:

R = H, CH_3, CH_2–CH_3, CH=CH_2, C≡CH, isopropyl (Pr^i),
tert-butyl (Bu^t).
R = Cl, CH_2Cl, $CHCl_2$, CCl_3.
R = F, CH_2F, CHF_2, CF_3.

Conjugate bases of these structures were obtained by removal of the cage H-atom.[16]

The geometries of acidic and basic forms in both series were fully optimised at the semi-empirical AM1 level of theory.[27] Energy and property evaluations were then performed at the *ab initio* HF/3-21G[28] level in a single point direct-SCF calculation on the AM1 optimized structures. This basis set was chosen as it has been shown to yield relatively good quality/cost ratios for both Hartree–Fock and Density Functional Theory[29] methods.[30]

The notation used in this study is the IUPAC notation.[31]

The charges on the different atoms for all systems under consideration were also calculated. The charge on an atom K is obtained by subtracting the Mulliken population N_k[32] from its nuclear charge Z_k.

From the Mulliken populations obtained we also calculated the electronic delocalisation, Δ, as introduced in our previous work[15,16] and expressed in terms of the fractional number of electrons vanishing from the C-atom (which carries the acidic proton) upon deprotonation of the acid.

The quantity Δ is then given by eqn. (1) where $N_C(n)$, $N_H(n)$

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

and $N_C(n-1)$ are the Mulliken populations at the C and H atoms of the acidic system and at the same, and thus deprotonated, C atom of the conjugate base, respectively.[15,16]

All calculations were performed with the MNDO94[33] and the GAUSSIAN94[34] programs on the CRAY J916/8-1024 computer of the Free Universities of Brussels combined with the UniChem software package[35] on a Silicon Graphics ONYX Extreme workstation.

Results and discussion

In order to sketch the delocalisation resulting from the deprotonation of the acidic compound, we analysed the charges and the geometries of all the systems, acidic as well as basic forms. Furthermore, we have calculated the differences of atomic charges and bond lengths between the basic and the acidic forms.

A number of results will be shown on planar graphs of C_{60} where, instead of the more traditionally used Schlegel diagrams, the protonated 6 : 6 ring fusion is taken as centre of the plot. For brevity we show only a representable selection of plots.†

Table 1 Charge on the acidic H atom, q_H, charge delocalised to the system upon deprotonation and electronic delocalisation Δ for the hydrofullerenes (all values in a.u.)

Hydrofullerene	q_H	Delocalised charge	Δ
$C_{60}H_2$	0.2895	0.7105	0.9917
$C_{60}H_4$	0.2874	0.7126	0.9975
$C_{60}H_6$	0.2836	0.7164	0.9970
$C_{60}H_8$	0.2797	0.7203	0.9979
$C_{60}H_{10}$	0.2778	0.7222	1.0031
$C_{60}H_{12}$	0.2744	0.7256	1.0073

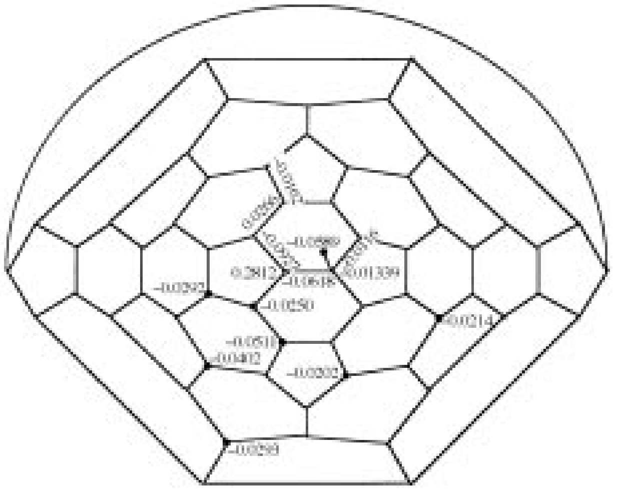

Fig. 1 Planar graph of 1,2-$C_{60}H_2$ giving the significant charge differences in the lower half, together with significant bond length differences in the upper half (all values in a.u.)

General aspects

For the series of hydrogenated fullerenes a charge of *ca.* 0.28 a.u. was found for the most acidic H atom. These values are given in Table 1 together with the electronic delocalisation Δ and the amount of charge delocalised to the rest of the system upon deprotonation (values taken from ref. 15). From the calculated values for the electronic delocalisation we can see that approximately one electron is delocalised from the deprotonated C atom, indicating that the deprotonated C atom loses more charge than at first absorbed from the H atom, *i.e.* the charge delocalises from C after deprotonation, in contradiction to earlier predictions, based on AM1 calculations.[36] Indeed one might expect this charge to have remained localised on this C atom, because on protonating the conjugate base, the H atom will regain its former place, in view of the acid–base equilibrium.[36] However, for systems behaving as conjugated alkenes (see, for example, ref. 3), delocalisation can easily follow the path of bond alternation, both on deprotonation and reprotonation (*vide infra*).

In Table 2 the charges are listed for acidic and basic forms of the hydrofullerenes: for the deprotonated C atom, for its neighbour carrying the second (remaining) H atom, and for this H atom in the acidic and basic form, together with the charge difference upon deprotonation. The differences are calculated as the difference between the basic and acidic form, a negative value thus meaning that the atom has absorbed more charge upon deprotonation. From Table 2 we can see that the adjacent C atom takes a little charge after delocalisation, but the bonded H atom takes almost double charge. Although this charge absorbance is very small, this H atom is in fact the atom taking the most charge in the whole system after deprotonation. This is illustrated in Fig. 1, where we have plotted the charge differences for the atoms for 1,2-$C_{60}H_2$ (atoms without a value have a charge difference less than 0.001 a.u.). In Fig. 2 the atoms are numbered in decreasing order of charge absorbed. In this way

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† A complete set of diagrams can be obtained upon request from the authors.

Table 2 Charge differences (acid–base) for relevant atoms (all values in a.u.). Note that negative values indicate more charge in the conjugate base.

	C deproton.	C adjacent	H adjacent	all H atoms	1 pyracylene	cage
$C_{60}H_2$ acid	−0.3113	−0.3113	0.2895	0.2895	−0.2273	−0.5790
base	−0.0300	−0.3452	0.2306	0.2306	−0.2822	−1.2306
difference	**0.2813**	**−0.0339**	**−0.0589**	**−0.0589**	**−0.0549**	**−0.6516**
$C_{60}H_4$ acid	−0.3123	−0.3126	0.2850	0.8558	−0.2877	−1.1432
base	−0.0275	−0.3484	0.2277	0.7344	−0.3400	−1.7344
difference	**0.2848**	**−0.0358**	**−0.0573**	**−0.1214**	**−0.0523**	**−0.5912**
$C_{60}H_6$ acid	−0.3114	−0.3113	0.2812	1.4106	−0.2989	−1.6942
base	−0.0309	−0.3477	0.2236	1.2292	−0.3595	−2.2292
difference	**0.2805**	**−0.0364**	**−0.0576**	**−0.1814**	**−0.0606**	**−0.5350**
$C_{60}H_8$ acid	−0.3112	−0.3113	0.2821	1.9595	−0.3065	−2.2392
base	−0.0336	−0.3427	0.2210	1.7169	−0.3831	−2.7169
difference	**0.2776**	**−0.0314**	**−0.0611**	**−0.2426**	**−0.0766**	**−0.4777**
$C_{60}H_{10}$ acid	−0.3119	−0.3119	0.2778	2.4943	−0.3649	−2.7721
base	−0.0310	−0.3446	0.2175	2.1901	−0.4377	−3.1901
difference	**0.2809**	**−0.0327**	**−0.0603**	**−0.3042**	**−0.0728**	**−0.4180**
$C_{60}H_{12}$ acid	−0.3117	−0.3117	0.2744	3.0185	−0.3741	−3.2929
base	−0.0300	−0.3449	0.2136	2.6537	−0.4547	−3.6537
difference	**0.2817**	**−0.0332**	**−0.0608**	**−0.3648**	**−0.0806**	**−0.3608**

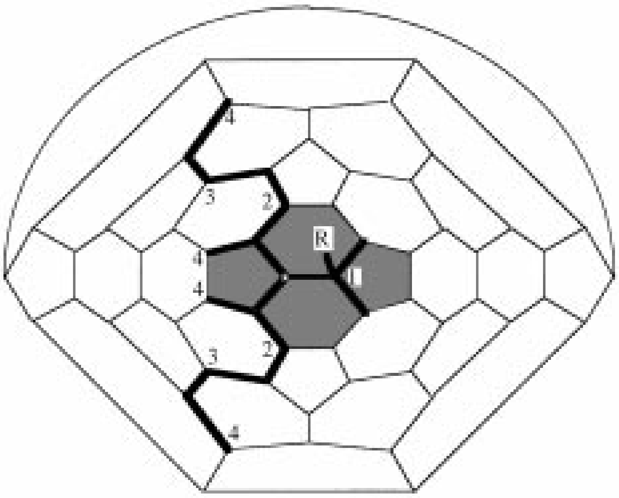

Fig. 2 Planar graph of 1,2-$C_{60}H_2$ representing the delocalisation pattern (see text); the pyracylenic unit around the protonated bond has been shaded

the delocalisation pattern can be followed: the three bonds shared by the deprotonated C atom are shortened, thus taking a more double character. Their six neighbours will then be elongated as compared to the acidic form, taking the negative charge over to the next atom. This delocalisation pattern can be achieved through the conjugation of the alternating bonds of the cage. For the C atoms themselves, the adjacent atom absorbs most of the charge, followed by the one in position ‘2’, then by ‘4’ and ‘6’. The same delocalisation path was found at the HF/6-31G*//AM1 level.

For the series $C_{60}H_2$ to $C_{60}H_{12}$ some general trends can be observed. First, the H atom neighbouring the deprotonated site absorbs more negative charge than any other atom of the cage. We can see from Table 2 that the values per atom are, however, very low. The negative charge resulting after deprotonation will be dispersed over the whole cage. Hence most of the charge will be absorbed by the cage, with the remaining H atoms each taking approximately as much charge as the α-C (0.03 a.u.), irrespective of their position of attachment to the cage. No evidence was found for benzenoid rings between the protonated pyracylenic units.

In order to get an idea of where the charge goes, we summed the charges for all but the most acidic H atom, for both acid and basic forms. These values and their differences are also given in Table 2, together with the summed charges for all atoms (again except the acidic H) of the ‘active’ (*i.e.* deprotonated) pyracylenic unit, and for all C atoms of the fullerene cage. We can see from these results that the set of H atoms together take more and more charge (though less per atom), even though the charge acceptance of the cage diminishes with greater hydrogenation level. The falling charge acceptance is due to the facts that (i) the overall charge of the cage is increasing in both acidic and basic forms and (ii) the higher number of hard H atoms on the cage decreases it overall charge capacity, with less charge stabilisation as a result.[15,16] The local charge absorbance of the deprotonated pyracylenic unit increases slightly, but most of the delocalising charge goes outside this unit. In fact no distinct sites of charge concentration are found, but rather a wide dispersal over the whole of the cage. It is this result that perhaps can be seen as the most surprising: delocalisation proceeds well beyond two or three bonds.

The delocalisation on deprotonation was analysed in the same way for a series of substituted hydrofullerenes. For this series of systems the same general features of the delocalisation are found as for 1,2-$C_{60}H_2$. Despite the diversity of functional groups considered, the charge on the acidic H atom is seen not to vary much throughout the series.[16] Also, the amount of negative charge delocalising from the deprotonated C atom in the conjugate bases does not seem to be influenced by the properties of the functional groups on the adjacent C atom (see the values of Table 2 in ref. 16). The deprotonated C atom again loses more charge after delocalisation than gained from the deprotonating H atom, as was the case for the hydrofullerenes. The charges of the functional groups are given in Table 3, together with the charges for the deprotonated C atom and the adjacent C atom carrying the functional group. Notwithstanding the fact that approximately one electron delocalises from the deprotonated C atom, less than one tenth of this charge is absorbed by the adjacent functional group, ranging from −0.022 to −0.106 electrons. The effect of the properties of the different functional groups is however clearly reflected in the charges for the functional groups in the acidic and basic forms. The charge acceptance tells us simply that little more charge is absorbed by the functional group after deprotonation. In the acidic form, a charge exchange between the functional group and the rest of the system has already taken place. Hence the functional group can be considered to be saturated with charge; the fullerene cage will act as an electron container, permitted by its great softness, and take most of the delocalised charge (*cf.* Table 3). Little charge is absorbed within this pyracylenic unit, most being delocalised over the whole of the cage.

Although the delocalisation upon deprotonation is different

Table 3 Charge differences for relevant atoms in alkyl- and fluoro- and chloro-alkyl substituted hydrofullerenes (see text; all values in a.u.)

	C deproton.	C adjacent	Func. group	1 pyracylene	cage
CH_3 acid	−0.2785	−0.3173	0.170	−0.2264	−0.4608
base	0.0257	−0.3648	0.105	−0.2852	−1.105
difference	**0.3042**	**−0.0475**	**−0.065**	**−0.0588**	**−0.6442**
CH_2–CH_3	−0.2783	−0.2849	0.154	−0.2164	−0.4458
	0.0312	−0.3425	0.084	−0.2856	−1.084
	0.3095	**−0.0576**	**−0.070**	**−0.0692**	**−0.6382**
$CH{=}CH_2$	−0.2846	−0.3783	0.181	−0.2184	−0.4702
	0.0180	−0.4386	0.110	−0.4068	−1.110
	0.3026	**−0.0603**	**−0.071**	**−0.0789**	**−0.6398**
$C{\equiv}CH$	−0.2744	−0.4562	0.170	−0.2491	−0.4836
	0.0326	−0.5434	0.129	−0.3237	−1.129
	0.3070	**−0.0872**	**−0.041**	**−0.0746**	**−0.6454**
Pr^i	−0.2842	−0.2519	0.130	−0.2127	−0.4218
	0.0256	−0.3103	0.050	−0.2896	−1.050
	0.3098	**−0.0584**	**−0.080**	**−0.0769**	**−0.6282**
Cl	−0.2575	−0.5312	0.145	−0.2733	−0.4699
	0.0614	−0.5703	0.039	−0.3728	−1.039
	0.3189	**−0.0391**	**−0.106**	**−0.0995**	**−0.5691**
CH_2Cl	−0.2800	−0.2913	0.063	−0.3011	−0.3549
	0.0223	−0.3589	−0.010	−0.3349	−0.9900
	0.3023	**−0.0676**	**−0.073**	**−0.0338**	**−0.6351**
$CHCl_2$	−0.2849	−0.2623	−0.035	−0.2894	−0.2726
	0.0287	−0.3366	−0.120	−0.3614	−0.8800
	0.3136	**−0.0743**	**−0.085**	**−0.0720**	**−0.6074**
CCl_3	−0.2903	−0.2302	−0.130	−0.3200	−0.1954
	0.0372	−0.3087	−0.226	−0.3807	−0.7742
	0.3275	**−0.0785**	**−0.096**	**−0.0607**	**−0.4584**
F	−0.3636	0.3429	−0.379	−0.3218	0.0537
	−0.0700	0.2778	−0.401	−0.3540	−0.599
	0.2936	**−0.0651**	**−0.022**	**−0.0322**	**−0.6527**
CH_2F	−0.2944	−0.3913	0.179	−0.2494	−0.4660
	0.0054	−0.4517	0.119	−0.3234	−1.119
	0.2998	**−0.0604**	**−0.060**	**−0.0740**	**−0.6530**
CHF_2	−0.2984	−0.4463	0.165	−0.3000	−0.4722
	0.0090	−0.5204	0.107	−0.3550	−1.107
	0.3074	**−0.0741**	**−0.058**	**−0.0550**	**−0.6348**
CF_3	−0.2986	−0.4869	0.122	−0.3438	−0.4430
	0.0283	−0.5781	0.065	−0.3887	−1.065
	0.3269	**−0.0912**	**−0.057**	**−0.0449**	**−0.6220**

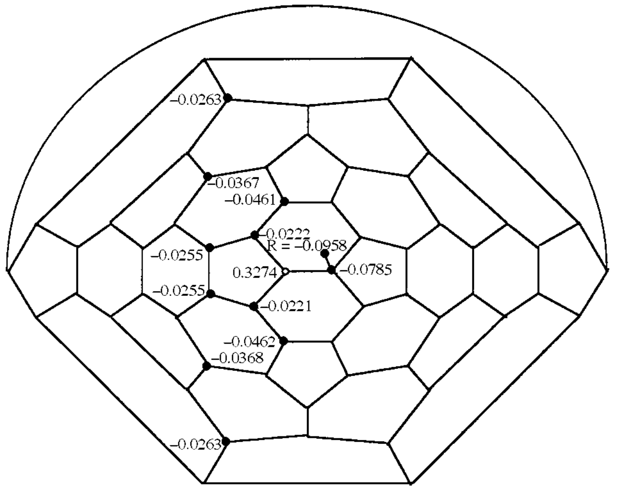

Fig. 3 Planar graph of 1,2-$C_{60}HCCl_3$ giving the significant charge differences (all values in a.u.)

in detail for every system due to the influence of the functional group, the patterns are the same as for 1,2-$C_{60}H_2$, as given in Fig. 2. In Fig. 3 the relevant charge differences for the atoms of $C_{60}HCCl_3$ are given. We can see by comparing with Fig. 1 the same general trends, namely, the deprotonated C atom loses more charge than received from the deprotonating H atom, as indicated by the high Δ value. This charge is delocalised mainly to the same atoms as in Fig. 2, following the same delocalisation path as for 1,2-$C_{60}H_2$. Significant differences are seen only for the adjacent C atom and the functional group, taking more charge than the H atom and stabilising twice as much charge on the adjacent C atom as in 1,2-$C_{60}H_2$ (for more details on the properties of the different functional groups, see refs. 16 and 37). Similar results were found for the whole of the series of substituted hydrofullerenes considered. It is rather surprising that the identity of the functional group does not influence this delocalisation more. The influence of the functional group is already explicit in the acidic form. Significant differences in the charge distribution can be seen when comparing these for the different groups. On deprotonation of the cage, however, this distribution will obey the different delocalisation paths given by the structure and bond alternation of the cage, whereas the functional group can influence this delocalisation only by its different charge acceptance, governed by its electronegativity and chemical hardness,[16] and its ability to stabilise negative charge on the C atom adjacent to the deprotonation site.

Let us return to the question of why, apparently, the charge resulting from the deprotonation does not stay localised on the deprotonated C atom. This C atom is sp^3 hybridised in the acidic form. It has been suggested that a partial sp^3 hybridisation remains in the basic form, with the C atom remaining relatively pyramidal. However, inspection of the (optimised) structure of the basic form shows the deprotonated C atom to be even less pyramidal than the other C atoms of the cage. Finally, the main argument for the charge remaining localised on the deprotonated C atom is the fact that on again protonating (or functionalising) the system, the 1,2-isomer is again found.[36] The high polarisability of the cage and the given alternating conjugated bond structure can however permit delocalisation in both ways. It is reasonable to speculate that upon approach of the addend, the electron density will be influenced

Table 4 Charge on the acidic H atom, charge delocalised to the system upon deprotonation and electronic delocalisation Δ for the selected hydrofullerenes (all values in a.u.)

	q_H	Delocalised charge	Δ delocalisation
1,2-$C_{60}H_2$	0.2951	0.7049	0.9707
1,2-$C_{70}H_2$	0.2989	0.7011	0.9818
1,*2*-$C_{70}H_2$	0.2950	0.7050	0.9671
5,6-$C_{70}H_2$	0.2971	0.7029	0.9853

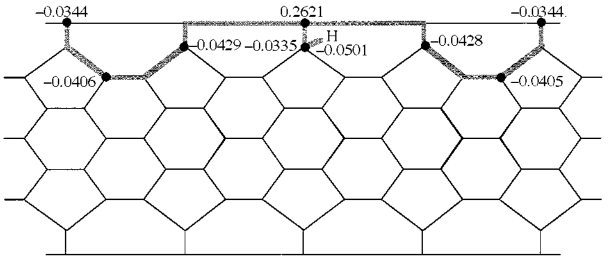

Fig. 4 Planar graph (see text) of 1,*2*-$C_{70}H_2$ depicting the significant charge differences (all values in a.u.)

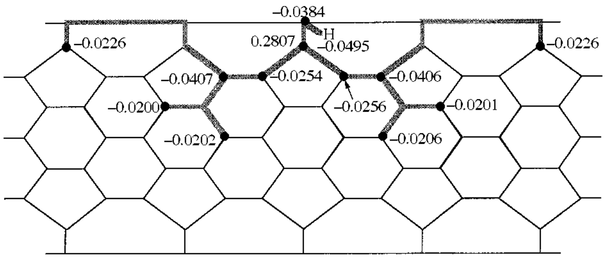

Fig. 5 Planar graph (see text) of *1*,2-$C_{70}H_2$ depicting the significant charge differences (all values in a.u.)

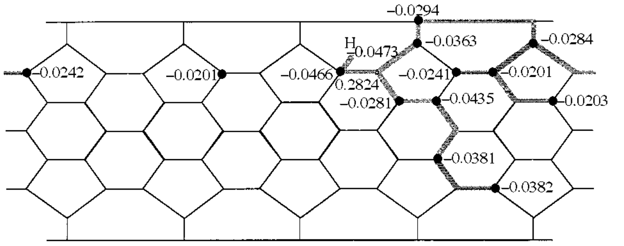

Fig. 6 Planar graph (see text) of 5,6-$C_{70}H_2$ depicting the significant charge differences (all values in a.u.)

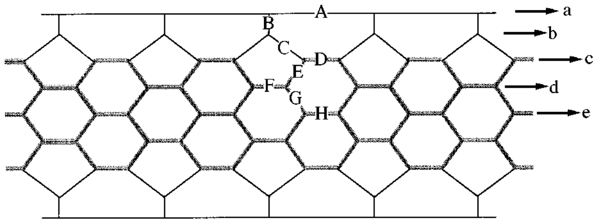

Fig. 7 Planar graph (see text) of C_{70} in which the different types of bonds (A–H) and atoms (a–e) are indicated

in such a way that the 1,2-isomer forms. It would be more surprising if high charges remained localised, in view of the conjugated bond structure and the stabilisation of the conjugate base by delocalisation.

Application: acidity of $C_{60}H_2$ *versus* $C_{70}H_2$: influence of delocalisation

As a final application we analysed the acidity of $C_{60}H_2$ as compared to $C_{70}H_2$. Although an experimental pK_a value has been determined only for $C_{60}H_2$,[38] some predictions have been made for the acidity of $C_{70}H_2$ based only on ^{1}H NMR findings.[39,40] What is seen in the ^{1}H NMR experiment is the smaller electron-withdrawing effect of the C_{70} cage compared to the C_{60} cage,[11] resulting in more positively charged H atoms on the cage. However, if by means of extended delocalisation, the $C_{70}H^-$ conjugate base were more stabilised than the $C_{60}H^-$ cage, this could counter the effect of the lower electron affinity of the cage and make $C_{70}H_2$ a more acidic system than $C_{60}H_2$, as predicted by our calculations.[15]

In order to settle this point we have studied the deprotonation energies of the two most stable $C_{60}H_2$ isomers, namely 1,2-$C_{60}H_2$ and 1,4-$C_{60}H_2$,[41] in comparison with the two most stable isomers of $C_{70}H_2$, namely 1,2-$C_{70}H_2$ and 5,6-$C_{70}H_2$.[39] Deprotonation of 1,2-$C_{70}H_2$ results in two different conjugate bases since the H atoms are inequivalent; we will use a notation in which the deprotonated H atom is italicised *e.g.* *1*,2-$C_{70}H_2$ resulting from the deprotonation of the H atom at position 1. We have calculated the (gas-phase) deprotonation energies for the isomers of $C_{60}H_2$ and $C_{70}H_2$ under consideration,[15,16] at the HF/3-21G//HF/3-21G level of theory, and obtained the following sequence (values in kcal mol^{-1}):

1,4-$C_{60}H_2$	<	5,6-$C_{70}H_2$	≈	*1*,2-$C_{70}H_2$	<	1,2-$C_{60}H_2$	≈	1,*2*-$C_{70}H_2$
337.44		338.81		338.96		345.23		345.63

which permits a clear distinction of the calculated acidities (the results given here for 1,2-$C_{60}H_2$ will therefore show small differences from the results given earlier, calculated on AM1 optimised structures, but their size shows the AM1 optimisations to be reliable for this kind of system). We can see that the lowest deprotonation energy is for the 1,4-$C_{60}H_2$ isomer. In fact, since the conjugate base of all $C_{60}H_2$ isomers is the same $C_{60}H^-$ structure, and the acidic forms of other isomers are less stable, even lower deprotonation energies will be found when considering any other $C_{60}H_2$ isomer than 1,2-$C_{60}H_2$.

In Table 4 the charges for the acidic H atom are given, q_H, together with the amount of charge transfer resulting from the deprotonation and the calculated Δ value. The lower electron-withdrawing effect of the C_{70} cage as compared to C_{60}[7] is seen to be translated into the more positively charged H atom for the $C_{70}H_2$ isomers (for 1,2-$C_{70}H_2$, the sum of charges on both H atoms has to be compared). Also, more charge will delocalise from the deprotonated C atom for *1*,2-$C_{70}H_2$ and 5,6-$C_{70}H_2$ as shown by the Δ values.[15,16] In Table 5 the charges for the acidic and basic form, together with their difference, are given for the deprotonated C atom, its hydrogen-bearing neighbour and the β-H atom, for the 1,2-$C_{60}H_2$ and the $C_{70}H_2$ isomers. The deprotonated C atom will be less, and the adjacent C atom more charged in the $C_{70}H_2$ isomers than in $C_{60}H_2$. We have also calculated the charges for the protonated pyracylenic unit in the acidic and basic form together with their difference, given in Table 5. The pyracylenic units in 1,2-$C_{60}H_2$ and 1,*2*-$C_{70}H_2$ are seen to take some charge upon deprotonation. Upon deprotonation of the '*1*' H atom, however, the same unit will lose charge. Even more charge is lost in 5,6-$C_{70}H_2$. To visualise this difference in delocalisation, we have plotted the values of the charge differences greater than 0.02 a.u. for the three isomers of $C_{70}H_2$ on planar graphs (see Figs. 4–6). The band of hexagonal rings is in the middle of the picture and the 'top' and 'bottom' pentagons of C_{70} coincide with the top and the bottom of the graph, as shown in Fig. 7 where this equatorial band has been depicted by grey lines. In Fig. 7 the different bonds (A–H) and C atoms (a–e) are also shown. From the positions of the atoms taking most charge on deprotonation, a delocalisation path can be found, given in heavy grey lines. The delocalisation path found for 1,*2*-$C_{70}H_2$ (Fig. 4) is very similar to the one found for 1,2-$C_{60}H_2$ (see Figs. 1 and 2). No significant delocalisation is found towards the equatorial band. Again, the atoms at the '2', '4' and '6' positions take most charge. A different pattern is, however, found for the *1*,2-$C_{70}H_2$ system, where more charge is delocalised to the equatorial band. The most significant difference

Table 5 Charge differences (base–acid) for relevant atoms of the $C_{70}H_2$ isomers under consideration (all values in a.u.). Note that negative values indicate more charge in the conjugate base.

	C deproton.	C adjacent	H adjacent	1 pyracylene
1,2-$C_{60}H_2$ acid	−0.2977	−0.2977	0.2951	−0.5289
base	−0.0319	−0.3315	0.2411	−0.5314
difference	**0.2658**	**−0.0338**	**−0.0540**	**−0.0025**
1,2-$C_{70}H_2$ acid	−0.3007	−0.3007	0.2950	−0.4845
base '*1*'	−0.0200	−0.3390	0.2455	−0.4585
difference	**0.2807**	**−0.0384**	**−0.0495**	**0.0260**
1,2-$C_{70}H_2$ acid	−0.3007	−0.3007	0.2950	−0.4845
base '*2*'	−0.0386	−0.3342	0.2449	−0.4924
difference	**0.2621**	**−0.0335**	**−0.0501**	**−0.0079**
5,6-$C_{70}H_2$ acid	−0.2994	−0.2994	0.2971	−0.5289
base	−0.0170	−0.3460	0.2498	−0.4885
difference	**0.2824**	**−0.0466**	**−0.0473**	**0.0404**

from the earlier delocalisation patterns is seen for 5,6-$C_{70}H_2$ (see Fig. 6), where the equatorial band of hexagonal rings absorbs even more charge (these patterns do not differ from the delocalisation pattern depicted in Fig. 2 when taking the different bond orders into consideration[42]). This delocalisation results in a different stabilisation of the conjugate base and explains the lower deprotonation energies found for 5,6-$C_{70}H_2$ and *1*,2-$C_{70}H_2$ compared to 1,*2*-$C_{70}H_2$ and 1,2-$C_{60}H_2$. The charge resulting from the deprotonation in 1,*2*-$C_{70}H_2$ cannot reach the equatorial belt as easily as in the former two isomers. This will result in a better stabilisation of the conjugate base, and hence a lower deprotonation energy. These differences, being properties of the conjugate base, cannot be predicted from the acidic form through, for example, the charges on the acidic H atom. Indeed, as seen in Table 4, the trend of the values for q_H is not translated completely in the acidity trend. This further confirms that caution has to be exercised in describing the acidity of the hydrofullerenes by taking only the acidic forms into account. For the description of the acidity of $C_{70}H_2$ as compared to $C_{60}H_2$, this approach would clearly fail.

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