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Quantum Chemical Study of the Reactivity of $C_{60}HR$ and $C_{60}(CHR)$ Derivatives

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In the present work a quantum chemical study of a series of substituted hydrofullerenes, $C_{60}HR$, and a series of methanofullerenes, $C_{60}(CHR)$, is presented. Their reactivity and geometrical, energetic, electronic, and magnetic properties, as well as the influence of the substituent, are discussed. As a probe of the reactivity, the acidic properties of these fullerene derivatives were predicted, based on the calculated deprotonation energies, with a previously set up scheme. The electronic delocalization upon deprotonation was described, and the global (magnetizabilities) and local aromaticity (nucleus-independent chemical shifts) was analyzed and compared with respect to the group properties for the series of functional groups. The geometries of both acidic and basic forms were fully optimized at the AM1 level, and all property calculations were performed at the HF/3-21G and the B3LYP/6-31G* level of theory.

I. Introduction

In fullerene chemistry, addition reactions are the most important route to functionalization, leading to a whole range of organic reactions.[1−5] In this study, two types of addition products are considered: a series of substituted hydrofullerenes, $C_{60}HR$ (which are systems derived from 1,2-$C_{60}H_2$ by substituting one hydrogen atom by a functional group) and a series of methanofullerenes, $C_{60}(CHR)$ (which are systems derived from the formal addition of a carbene fragment), with 10 distinct functional groups.

Substituted hydrofullerenes $C_{60}HR$ are of special interest for their acidic properties, which can be tailored by the variation of the functional group R.[6] Furthermore, these systems can serve as precursors for further functionalization of C_{60}, based on these acidic properties and the high thermodynamic stability of the conjugated bases.[7,8] While the methanofullerenes $C_{60}(CHR)$ are one of the most versatile and widely studied class of fullerene adducts,[4] the question remains if the acidity could also be used here as a tool for further functionalization of these systems. For substituted hydrofullerenes, addition takes place preferentially at the more reactive [6,6]-ring junctions, rather than at the longer [5,6]-bonds,[1,9,10] but in case of carbene addition to C_{60}, four possible ways exist to add a one-carbon bridge across a carbon−carbon bond. Of these, only the [5,6]-open methanofulleroids (methanoannulenes)[11−15] and the [6,6]-closed methanofullerenes (cyclopropane derivatives),[16] which are the two stable isomers,[17] have been experimentally observed. Addition of carbene transfer reagents such as diazo compounds to C_{60} often generates the [5,6]-open fulleroid as the kinetically controlled product, while the thermodynamically controlled product is the [6,6]-closed methanofullerene. Upon heating, the mixture of [6,6]-closed and [5,6]-open isomers formed together in the course of the synthesis are converted exclusively to the most stable [6,6]-closed isomer. The rearrangement from [5,6]-open

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(1) Hirsch, A. *The Chemistry of the Fullerenes*; Georg Thieme Verlag: Stuttgart, 1994.

(2) Taylor, R. *The Chemistry of Fullerenes*; World Scientific Pub Co.: River Edge, NJ, 1996.

(3) Taylor, R. *Lecture Notes on Fullerene Chemistry. A Handbook for Chemists;* Imperial College Press: London, 1999.

(4) Diederich, F.; Isaacs, L.; Philip, D. *J. Chem. Soc.-Perkin Trans. 2* **1994**, 391.

(5) Diederich, F.; Thilgen, C. *Science* **1996**, *271*, 317.

(6) Van Lier, G.; Safi, B.; Geerlings, P. *J. Phys. Chem. Solids* **1997**, *58*, 1719.

(7) Kitagawa, T.; Tanaka, T.; Murakita, H.; Nishikawa, A.; Takeuchi, K. *Tetrahedron* **2001**, *57*, 3537.

(8) Kitagawa, T.; Takeuchi, K. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 785.

(9) Hirsch, A. *Synthesis* **1995**, 895.

(10) Hirsch, A. In *Fullerenes and Related Structures, Topics in Current Chemistry;* Springer-Verlag: Heidelberg, Germany, 1999; Vol. 199.

(11) Prato, M.; Lucchini, V.; Maggini, M.; Stimpfl, E.; Scorrano, G.; Eiermann, M.; Suzuki, T.; Wudl, F. *J. Am. Chem. Soc.* **1993**, *115*, 8479.

(12) Wudl, F. *Acc. Chem. Res.* **1992**, *25*, 157.

(13) Suzuki, T.; Li, Q. C.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 7301.

(14) Smith, A. B.; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J.; Owens, K. G.; King, R. C. *J. Am. Chem. Soc.* **1993**, *115*, 5829.

(15) Isaacs, L.; Wehrsig, A.; Diederich, F. *Helv. Chim. Acta* **1993**, *76*, 1231.

(16) Diederich, F.; Isaacs, L.; Philp, D. *Chem. Soc. Rev.* **1994**, *23*, 243.

(17) Diederich, F.; Rubin, Y. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1101.

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fulleroid to [6,6]-closed fullerene has been studied both experimentally[11,15,18] and theoretically.[4]

In the present study we will analyze the difference in geometry and electronic structure between a series of substituted hydrofullerenes and methanofullerenes, with different functional groups [R = H, OH, OCH_3, NH_2, $NHCH_3$, $N(CH_3)_2$, CH_3, $CH{=}CH_2$, C_6H_5 (further referred to as Ph), and $C{\equiv}CH$], in both their acidic [$C_{60}HR$ and $C_{60}(CHR)$] and basic [$C_{60}R^-$ and $C_{60}(CR^-)$] forms. For all the systems, only the thermodynamically preferred [6,6]-adduct is analyzed. Differences in geometrical and energetic characteristics are presented between the series, and the influence of the different functional groups is addressed. As a probe of the reactivity, their acidity is predicted using a previously set up scheme.[19] Also the global and local aromaticity is studied for the whole series under consideration, to further discuss the reactivity of these fullerene derivatives. Because the chemistry of the fullerenes is suggested to proceed in such a manner that the reaction products become as aromatic as possible, the analysis of the global and local aromaticity of the products can give important information about the reactivity and the addition patterns for fullerenes.[20,21] We have performed NICS calculations at all geometrical ring centers for all systems [$C_{60}HR$, $C_{60}R^-$, $C_{60}(CHR)$, and $C_{60}(CR^-)$]. Nucleus-independent chemical shifts (NICS)[22] are computed reliably with modern quantum-chemical methods and afford a simple and efficient probe of the local aromatic properties.[23,24]

In the next section we present the theoretical and computational details. In section III, the geometrical, energetic, electronic, and magnetic features are analyzed to understand the influence of the substituent with respect to the deprotonation process of the systems under consideration and to discuss the different acidic character between series of substituted hydrofullerenes and methanofullerenes. Conclusions are drawn in section IV.

II. Theoretical and Computational Details

The geometries of acidic and basic forms in both series, $C_{60}HR$ and $C_{60}(CHR)$, were fully optimized at the semiempirical AM1 level of theory[25] using the AMPAC program.[26] Two deprotonated forms were optimized for the $C_{60}(CR^-)$ series, with the functionalized bond remaining closed or opening upon addition, the so-called [6,6]-closed and [6,6]-open isomers. Starting from different bond lengths for the functionalized bond, full AM1 optimization yielded two structures in each case, with relative stabilities varying, and the bond length being significantly enlarged for one structure as compared to the other one. Single point calculations at the HF/3-21G and B3LYP/6-31G* levels were performed using GAUSSIAN98[27] at the AM1 fully optimized geometries. The AM1 method has been preferred to other semiempirical methods because it yields reliable results for geometries of C_{60} derivatives, as for example for Diels–Alder adducts.[28,29]

For each substituted hydrofullerene and each methanofullerene we calculated the (gas-phase) deprotonation energy, ΔE. As considered in our previous studies,[30] the deprotonation energy is defined as

$$\Delta E = E(\mathrm{A}^-) - E(\mathrm{AH}) \tag{1}$$

where $E(\mathrm{AH})$ and $E(\mathrm{A}^-)$ are respectively the total energy for the acidic form of these compounds and that of its conjugated base form.

We also calculated the charges on the different atoms for all the molecules. These charges were evaluated by a Mulliken population analysis,[31] in order to be comparable with our previous studies.[32] From these Mulliken populations, the electronic delocalization Δ is calculated, as introduced in our previous work.[19] This electronic delocalization is expressed in terms of the amount of electrons leaving the C atom carrying the acidic proton upon deprotonation of the acid. We define this quantity as

$$\Delta = [N_{\mathrm{C}}(n) - N_{\mathrm{H}}(n)] - N_{\mathrm{C}}(n-1) \tag{2}$$

where $N_{\mathrm{C}}(n)$, $N_{\mathrm{H}}(n)$, and $N_{\mathrm{C}}(n-1)$ are the Mulliken populations at the C and H atoms of the acidic system and at the same, thus deprotonated, C atom of its conjugate base, respectively.

Finally we analyzed the global aromaticity in terms of the molecular magnetizability for each structure, using the CSGT method,[33] and the local aromaticity is calculated at the geometrical centers of the ring, determined by the nonweighted mean of the ring atom coordinates, using the GIAO method.[34] The local aromaticity of a ring is described by its ability to support diamagnetic ring (i.e. diatropic) currents, which can be described by the nucleus-independent chemical shift or NICS.[22] Both, magnetizabilities and NICS values were calculated at the ab initio HF/3-21G level of theory using the AM1 fully optimized geometries.

III. Results and Discussion

Geometrical Analysis. Figure 1 shows the five different types of structures considered in this present study: the acidic forms of the substituted hydrofullerenes ($C_{60}HR$) and the methanofullerenes [$C_{60}(CHR)$] and their

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[18] Hall, M. H.; Lu, H.; Shevlin, P. B. *J. Am. Chem. Soc.* **2001**, *123*, 1349.

[19] Choho, K.; Van Lier, G.; Van De Woude, G.; Geerlings, P. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1723.

[20] van Lier, G.; De Proft, F.; Geerlings, P. *Phys. Solid State (Translation of Fizika Tverdogo Tela (Sankt-Peterburg))* **2002**, *44*, 588.

[21] Van Lier, G.; De Proft, F.; Geerlings, P. *Chem. Phys. Lett.* **2002**, *366*, 311.

[22] Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; van Eikema Hommes, N. J. R. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

[23] Van Lier, G.; Fowler, P. W.; De Proft, F.; Geerlings, P. *J. Phys. Chem. A* **2002**, *106*, 5128.

[24] De Proft, F.; Geerlings, P. *Chem. Rev.* **2001**, *101*, 1451.

[25] Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

[26] AMPAC 6.0, 1994 Semichem, 7128 Summit, Shawnee, KS 66216.

[27] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

[28] Solà, M.; Mestres, J.; Martí, J.; Duran, M. *Chem. Phys. Lett.* **1994**, *231*, 325.

[29] Mestres, J.; Duran, M.; Solà, M. *J. Phys. Chem.* **1996**, *100*, 7449.

[30] Damoun, S.; Langenaeker, W.; Van de Woude, G.; Geerlings, P. *J. Phys. Chem.* **1995**, *99*, 12151.

[31] Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833.

[32] Van Lier, G.; Safi, B.; Geerlings, P. *J. Chem. Soc., Perkin Trans. 2* **1998**, 349.

[33] Cheeseman, J. R.; Trucks, G. W.; Keith, T. A.; Frisch, M. J. *J. Chem. Phys.* **1996**, *104*, 5497.

[34] Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.

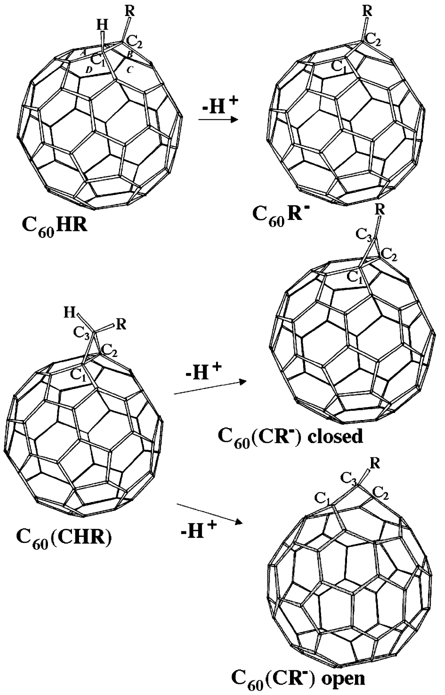
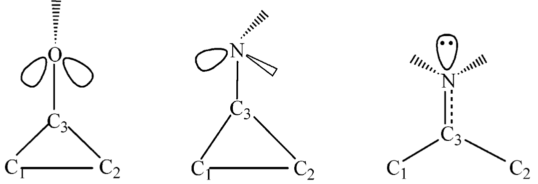


FIGURE 1. Atom labels for the substituted hydrofullerenes and methanofullerenes.

SCHEME 1. Three-Dimensional Representation of Atoms and Orbitals with Nonbonding Electrons



corresponding basic forms ($C_{60}R^-$) and both $C_{60}(CR^-)$ open and closed structures.

Relevant bond lengths [$d(C_1-C_2)$, $d(C_1-H)$, $d(C_2-R)$, $d(C_1-C_3)$, $d(C_2-C_3)$, and $d(C_3-R)$], as well as the value for the angle [$\alpha(C_1C_3C_2)$] resulting from the carbene addition are gathered in Table S1 of the Supporting Information, for the series of substituted hydrofullerenes and methanofullerenes.

We did not find a clear relation between the character of the R substituents and the change in geometry due to deprotonation in case of substituted hydrofullerenes, but two main tendencies can be discerned for the methanofullerene systems.

First, for the $C_{60}(CHR)$ and $C_{60}(CR^-)$ series, the $d(C_1-C_3)$ and $d(C_2-C_3)$ are identical in the case of the closed structures studied, except for $R = NR'_2$, where one bond length is larger than the other. The different behavior of systems with NR'_2 can be understood if one takes into account that the N atom has a pair of nonbonding electrons, so that the substituents of N are placed less symmetrically (the two R′ substituents are facing the C_2-C_3 bond) than in the case of other R substituents (the O atom also has nonbonding electrons, but the two pairs are placed symmetrically with respect to the C_1-C_3 and C_2-C_3 bonds). This is represented in Scheme 1. The elongation of the C_2-C_3 bond in $C_{60}CHNR'_2$ species may be attributed to hyperconjugation from the lone pair of the N atom to the $\sigma^*(C_2-C_3)$ molecular orbital. Meanwhile, for open structures the $d(C_2-C_3)$ is larger than the $d(C_1-C_3)$ in general, except for $R = NR'_2$. In this latter case, the lone pair is placed symmetrically in such a way that it can participate in the π structure (see Scheme 1).

Second, compared with the corresponding acidic form $C_{60}(CHR)$, the bond distances between the atoms of the carbene fragment and the two C atoms of C_{60} generally become shorter, especially for the open form for which these two bonds are expected to have partial double bond character (see Scheme 2). Also, when R is an OR′ or NR'_2 π-donor type substituent, the shortening is less important for the $C_{60}(CR^-)$ closed structures than in case of the $C_{60}(CR^-)$ open structures. The reverse effect is found in the case of the other substituents. Resonance structures of the type III and IV (see Scheme 2) are favored by the presence of π-donor substituents.

From this geometric analysis it emerges that the R substituent character shows some slight influence with respect to the geometrical reorganization of the system upon deprotonation. For both types of systems the deprotonation process has a different effect on the C_{60} structure. The C_{60} fragment in $C_{60}HR$ is geometrically more modified than for $C_{60}(CHR)$, as shown by the magnitude of $\Delta E(C_{60})_{def}$ [calculated as $\Delta E(C_{60})_{def} = EC_{60}^{fragment} - EC_{60}^{optimized}$; see Supporting Information, Table S1]. $\Delta E(C_{60})_{def}$ ranges from 40.8 to 53.5 kcal/mol for $C_{60}HR$ and from 27.3 to 29.2 kcal/mol for $C_{60}(CHR)$. After deprotonation, $\Delta E(C_{60})_{def}$ ranges from 24.7 to 33.9 kcal/mol for the $C_{60}R^-$ series, so the $C_{60}R^-$ systems partially recover the C_{60} structure [the $d(C_1-C_2)$ recovers partially its double bond character], whereas for the open $C_{60}(CR^-)$ systems, this process involves an important elongation of the C_1-C_2 bond with a more important rearrangement [$\Delta E(C_{60})_{def}$ for the closed $C_{60}(CR^-)$ systems ranges from 30.4 to 43.1 kcal/mol, whereas for the open $C_{60}(CR^-)$ isomers it ranges from 138.6 to 159.5 kcal/mol] and a significant change in bond lengths and electronic charge distribution.

Energetic Analysis. The deprotonation energies are given in Table 1 for both series considered, calculated at HF/3-21G and B3LYP/6-31G* levels of theory at the same geometry (full AM1 optimization). From these energy values it is clear that the deprotonation is an endothermic process for both systems.

The results for the two possible geometries of $C_{60}(CR^-)$ show the closed structures to be more stable at AM1 and B3LYP/6-31G*//AM1 levels of theory. According to the HF/3-21G//AM1 results, the open structures are the most stable for R = OH, OCH_3, $CH{=}CH_2$, Ph, and $C{\equiv}CH$. This is an artifact of the HF/3-21G//AM1 method, since the full optimization of a series of structures (R = H, OH, CH_3) at the HF/3-21G level shows a higher stabilization of the closed structures as compared to the corresponding open structures at this level of theory. In Scheme 2, a mechanism is proposed for the rearrangement that systems undergo upon deprotonation, where it is clear that the different localization of the negative charge upon deprotonation is the key to finally have a closed or open structure of the $C_{60}(CR^-)$ systems. We expected that this could be related to the donor or acceptor character of the R substituent, but the influence is weak.

SCHEME 2. Depiction of the Deprotonation Process in the Case of Methanofullerenes with the Open and Closed Structures of the Basic Form

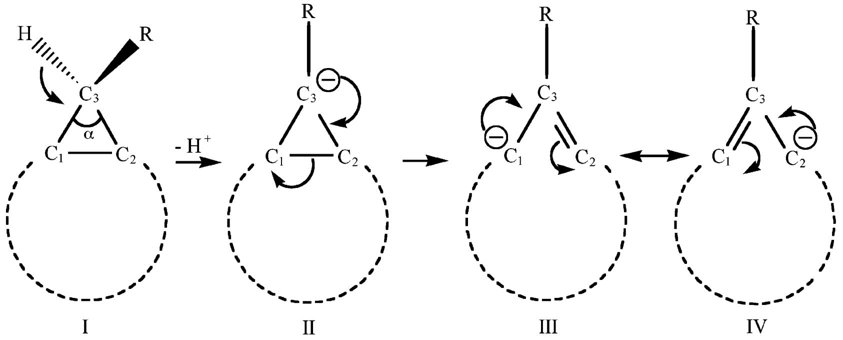


TABLE 1. Deprotonation Energy (au) at the HF/3-21G//AM1 and B3LYP/6-31G*//AM1 Levels for Each System, Calculated from the Energies of the Acidic (*E*(HA)) and Basic (*E*(A^-)) Form

$C_{60}HR/C_{60}R^-$	ΔE^a	ΔE^b
H	0.551287	0.525876
OH	0.543240	0.525220
OCH_3	0.543511	0.526113
NH_2	0.536352	0.537367
$NHCH_3$	0.545575	0.532816
$N(CH_3)_2$	0.556157	0.530520
CH3	0.511109	0.540212
$CH{=}CH_2$	0.545390	0.527624
Ph	0.540395	0.550336
C≡CH	0.542827	0.534062

$C_{60}CHR/C_{60}CR^-$	ΔE^a		ΔE^b	
	closed	open	closed	open
H	0.648125	0.647337	0.646160	0.596554
OH	0.613459	0.623578	0.604376	0.586769
OCH_3	0.612059	0.626793	0.610006	0.594606
NH_2	0.625752	0.609059	0.618732	0.594541
$NHCH_3$	0.620097	0.605464	0.628381	0.604377
$N(CH_3)_2$	0.621514	0.598748	0.606219	0.576850
CH_3	0.654385	0.650018	0.652242	0.615545
$CH{=}CH_2$	0.595032	0.612068	0.603465	0.599257
Ph	0.608776	0.627980	0.615395	0.603611
C≡CH	0.598421	0.620342	0.595362	0.591203

[a] HF/3-21G//AM1. [b] B3LYP/6-31G*//AM1.

TABLE 2. Electronic Delocalization Calculated from the Mulliken Populations ($N_{C\ acid}$, $N_{H\ acid}$ and $N_{C\ base}$) for All the Structures Studied at HF/3-21G//AM1

$C_{60}HR/C_{60}R^-$	$N_{C\ acid}$	$N_{H\ acid}$	$N_{C\ base}$	Δ
H	−0.311	0.290	−0.031	−0.570
OH	−0.303	0.332	0.010	−0.645
OCH_3	−0.302	0.332	−0.010	−0.624
NH_2	−0.280	0.310	−0.008	−0.581
NHCH3	−0.276	0.310	−0.011	−0.575
$N(CH_3)_2$	−0.274	0.314	−0.023	−0.566
CH_3	−0.279	0.291	0.026	−0.596
$CH{=}CH_2$	−0.270	0.300	0.035	−0.606
Ph	−0.267	0.311	0.051	−0.629
C≡CH	−0.274	0.314	0.032	−0.620

$C_{60}CHR/C_{60}CR-$	$N_{C\ acid}$	$N_{H\ acid}$	closed		open	
			$N_{C\ base}$	Δ	$N_{C\ base}$	Δ
H	−0.218	0.264	−0.290	−0.192	−0.017	−0.465
OH	0.346	0.283	0.336	−0.273	0.512	−0.449
OCH_3	0.357	0.252	0.378	−0.273	0.553	−0.448
NH_2	0.216	0.271	0.310	−0.365	0.529	−0.584
$NHCH_3$	0.248	0.269	0.347	−0.368	0.568	−0.589
$N(CH_3)_2$	0.273	0.265	0.360	−0.352	0.604	−0.596
CH_3	−0.100	0.265	−0.021	−0.344	−0.050	−0.315
$CH{=}CH_2$	−0.187	0.268	0.020	−0.475	−0.110	−0.345
Ph	−0.083	0.284	0.093	−0.460	−0.064	−0.303
C≡CH	−0.188	0.298	−0.007	−0.479	−0.182	−0.304

A prediction of the acidities (DMSO, 25 °C) for these systems is made from their theoretically calculated deprotonation energies, using a previously set up correlation scheme.[19] If we apply this correlation equation to the calculated deprotonation energies for both series, pK_a values are found for the substituted hydrofullerenes ranging from 2 to 7, whereas for the methanofullerenes the values range from 17 to 32, thus showing a higher acidic character for the series of substituted hydrofullerenes.

Electronic Analysis. The delocalization of the negative charge resulting from the deprotonation process also plays an important role in the stabilization of the conjugate base. From the values collected in Table 2, we can see that the electronic delocalization (Δ) is more important in the case of the substituted hydrofullerenes, but again from the results it is not possible to find a clear relation between delocalization and the character of the R substituent. These values are given at the HF/3-21G level of theory to be comparable with our previous results.[32] The B3LYP/6-31G*//AM-calculated delocalizations, given as Supporting Information in Table S2, show the same trend.

From the Mulliken charges for the atoms that belong to the reactive site (qR, qC_1, qC_2, qC_3, and qH) collected in Table S3, we have found that the charge originating from the deprotonation remains more localized in the addition region for the methanofullerenes as compared to the substituted hydrofullerene series. From the charges for the nonfunctionalized part of the cage q(58C) (see Table S3), which is the sum of the charges for the 58 nonfunctionalized carbon atoms of the cage, we can indeed see that less charge is delocalized for the closed methanofullerene basic forms as compared to the substituted hydrofullerenes basic forms. The higher charge to delocalize along the rest of the cage in the case of the substituted hydrofullerenes helps to provide a higher stabilizaton of the conjugated base structures, with a higher acidity as a result.

Aromaticity Analysis. As a measure of global aromaticity, the magnetizability χ_M of all systems under consideration have been calculated at the HF/3-21G level of theory (see Table 3). In almost all cases, the carbene system is found to be more aromatic as compared to its substituted hydrofullerene counterpart for the same

TABLE 3. Magnetizabilities (χ_M, in ppm cgs) and NICS (ppm cgs) for Selected Rings Calculated at HF/3−21G//AM1 Using the GIAO Method[a]

	χ_M	A	**B**	C	**D**	E	**F**	G	H	I	**J**	K	L
$C_{60}HR$													
H	−360	1.1	**0.7**	1.1	**0.7**	−9.4	**1.1**	−9.4	−7.8	−9.4	**1.1**	−9.4	−7.8
OH	−358	1.0	**1.6**	1.0	**0.9**	−9.3	**1.4**	−9.4	−7.9	−9.3	**1.4**	−9.3	−8.0
OCH_3	−366	0.9	**1.3**	0.9	**0.7**	−9.3	**1.4**	−9.2	−8.0	−9.2	**1.4**	−9.3	−8.1
NH_2	−362	1.0	**1.5**	1.2	**0.9**	−9.4	**1.1**	−9.4	−8.0	−9.3	**1.2**	−9.3	−8.0
$NHCH_3$	−367	1.0	**1.1**	1.1	**0.7**	−9.4	**1.1**	−9.5	−7.9	−9.1	**1.2**	−9.3	−8.0
$N(CH_3)_2$	−373	0.7	**1.3**	1.2	**0.8**	−9.3	**1.1**	−9.5	−8.0	−9.1	**1.1**	−9.3	−8.0
CH_3	−363	0.9	**1.0**	0.9	**1.0**	−9.4	**1.1**	−9.3	−7.9	−9.3	**1.1**	−9.4	−7.8
$CH{=}CH_2$	−364	1.0	**1.2**	1.0	**0.8**	−9.4	**1.1**	−9.1	−7.9	−9.3	**1.1**	−9.4	−7.9
Ph	−390	1.4	**1.8**	1.4	**0.9**	−9.3	**1.2**	−9.0	−7.9	−9.0	**1.2**	−9.3	−7.9
$C{\equiv}CH$	−366	0.9	**1.1**	0.9	**0.7**	−9.4	**1.1**	−9.4	−7.9	−9.4	**1.1**	−9.4	−8.0
$C_{60}R^-$													
H	−357	2.8	**3.7**	2.8	**−3.7**	−7.8	**−1.3**	−9.8	−4.4	−9.8	**1.3**	−7.8	−6.2
OH	−355	0.2	**5.6**	0.2	**−0.3**	−7.5	**1.0**	−9.4	−4.3	−9.4	**−1.0**	−7.5	−5.7
OCH_3	−359	−0.2	**5.4**	0.2	**0.4**	−7.5	**1.1**	−9.2	−4.5	−9.2	**−1.1**	−7.5	−5.7
NH_2	−358	0.2	**5.0**	1.0	**−1.6**	−7.7	**0.2**	−9.6	−4.5	−9.6	**0.5**	−8.1	−5.9
$NHCH_3$	−362	0.3	**4.8**	1.1	**−1.7**	−7.8	**0.3**	−9.4	−4.5	−9.5	**0.6**	−8.1	−5.9
$N(CH_3)_2$	−368	0.1	**5.0**	0.7	**−1.3**	−7.9	**0.4**	−9.4	−4.5	−9.4	**0.7**	−8.0	−5.9
CH_3	−361	1.7	**3.9**	1.7	**−2.7**	−7.9	**−0.8**	−9.7	−4.3	−9.7	**−0.8**	−7.9	−6.0
$CH{=}CH_2$	−361	1.6	**4.3**	2.1	**−2.8**	−7.9	**0.5**	−9.4	−4.4	−9.7	**−0.8**	−7.8	−6.0
Ph	−381	2.2	**5.2**	2.2	**−2.4**	−7.8	**0.3**	−9.4	−4.5	−9.3	**−0.3**	−7.8	−5.9
$C{\equiv}CH$	−362	1.7	**4.6**	1.7	**−2.9**	−8.0	**−0.5**	−9.7	−4.4	−9.7	**0.5**	−8.0	−6.1
$C_{60}CHR$													
H	−359	−4.2	**1.2**	−4.2	**1.2**	−8.8	**2.8**	−8.8	−7.3	−8.8	**2.8**	−8.8	−7.3
OH	−374	−3.9	**0.8**	−3.8	**0.8**	−8.8	**2.7**	−8.8	−7.4	−8.9	**2.4**	−8.9	−7.4
OCH_3	−365	−3.3	**1.0**	−4.0	**1.0**	−8.8	**3.0**	−8.7	−7.3	−8.9	**2.5**	−8.9	−7.3
NH_2	−369	−3.9	**0.8**	−3.6	**1.0**	−8.8	**2.6**	−8.8	−7.4	−8.9	**2.4**	−8.9	−7.3
$NHCH_3$	−373	−3.8	**0.7**	−3.5	**0.9**	−8.8	**2.6**	−8.9	−7.4	−8.9	**2.4**	−8.9	−7.3
$N(CH_3)_2$	−374	−2.7	**0.6**	−3.8	**1.1**	−8.8	**2.6**	−8.8	−7.4	−9.0	**2.4**	−8.9	−7.3
CH_3	−367	−4.5	**1.2**	−3.9	**1.2**	−8.8	**2.9**	−8.8	−7.3	−8.8	**2.6**	−8.8	−7.3
$CH{=}CH_2$	−366	−4.1	**1.2**	−3.9	**1.2**	−8.8	**2.8**	−8.8	−7.3	−8.8	**2.6**	−8.8	−7.3
Ph	−395	−4.0	**1.4**	−3.8	**1.4**	−8.8	**2.7**	−8.9	−7.3	−8.7	**2.7**	−8.7	−7.2
$C{\equiv}CH$	−370	−4.2	**1.2**	−4.3	**1.2**	−8.8	**2.9**	−8.8	−7.4	−8.8	**2.6**	−8.8	−7.4
$C_{60}CR^-$ closed													
H	−354	−1.2	**2.7**	−1.2	**2.7**	−8.7	**2.9**	−8.7	−6.8	−8.7	**2.9**	−8.7	−6.8
OH	−360	−2.2	**1.8**	−1.8	**1.8**	−8.8	**2.3**	−8.8	−6.5	−9.0	**1.7**	−9.0	−6.5
OCH_3	−366	−2.3	**1.8**	−2.0	**1.8**	−8.8	**2.4**	−8.8	−6.5	−9.0	**1.8**	−9.0	−6.5
NH_2	−367	−2.5	**1.9**	−1.0	**1.3**	−8.8	**1.8**	−9.0	−6.4	−9.2	**1.6**	−9.1	−6.6
$NHCH_3$	−372	−2.5	**1.8**	−1.0	**1.3**	−8.9	**1.9**	−9.0	−6.4	−9.2	**1.6**	−9.1	−6.7
$N(CH_3)_2$	−373	−1.5	**1.4**	−0.7	**1.6**	−8.9	**1.9**	−8.8	−6.7	−9.2	**1.8**	−9.2	−6.6
CH_3	−359	−1.3	**2.6**	−0.9	**2.6**	−8.6	**2.9**	−8.6	−6.8	−8.6	**3.0**	−8.6	−6.8
$CH{=}CH_2$	−365	−1.8	**2.0**	−1.8	**2.2**	−8.7	**2.8**	−8.7	−6.9	−8.7	**2.8**	−8.7	−6.9
Ph	−387	−1.8	**2.1**	−1.8	**2.1**	−8.6	**2.8**	−8.6	−6.9	−8.6	**2.8**	−8.6	−6.9
$C{\equiv}CH$	−366	−1.9	**2.1**	−1.9	**2.1**	−8.8	**2.7**	−8.6	−7.0	−8.8	**2.7**	−8.8	−7.0
$C_{60}CR^-$ open													
H	−355	4.1	**−0.8**	8.7	**9.4**	−8.9	**−2.6**	−7.3	−6.8	−6.4	**−6.4**	−9.7	−5.2
OH	−385	8.4	**−4.5**	14.1	**−0.0**	−10.7	**−7.5**	−9.5	−7.9	−9.4	**−11.2**	−10.8	−7.3
OCH_3	−389	8.8	**0.4**	14.0	**−4.5**	−9.4	**−8.3**	−10.6	−7.1	−10.9	**−12.0**	−9.3	−7.9
NH_2	−392	8.7	**−3.8**	11.7	**−3.8**	−10.6	**−10.0**	−10.6	−7.6	−10.6	**−11.7**	−10.6	−7.6
$NHCH_3$	−399	10.5	**−3.1**	8.6	**−4.0**	−10.6	**−11.3**	−10.6	−7.5	−10.6	**−10.2**	−10.6	−7.6
$N(CH_3)_2$	−405	9.3	**−3.5**	9.3	**−3.5**	−10.6	**−11.0**	−10.6	−7.5	−10.6	**−11.0**	−10.6	−7.5
CH_3	−361	3.5	**−0.0**	7.0	**9.0**	−9.0	**−2.3**	−7.5	−6.9	−7.0	**−5.9**	−9.9	−5.3
$CH{=}CH_2$	−350	−3.1	**5.7**	−3.2	**10.4**	−7.2	**2.0**	−6.8	−6.1	−6.8	**1.4**	−7.8	−5.1
Ph	−371	−5.7	**8.8**	−5.7	**8.8**	−6.9	**3.6**	−6.5	−5.6	−6.9	**3.6**	−6.5	−5.7
$C{\equiv}CH$	−348	−7.1	**9.0**	−7.0	**9.1**	−6.6	**4.4**	−6.2	−5.6	−6.6	**4.4**	−6.2	−5.6

[a] Bold type highlights the pentagonal rings.

functional group, and this for both the acidic and the basic forms. Generally, a slight decrease in global aromaticity can be seen upon deprotonation, coinciding with a lowered stability. For the methanofullerene series, a clear influence of the functional group can again be discerned in the basic form. Indeed, in case of an O- or N-containing functional group, a higher magnetizability can be found for the open structure, whereas the closed structure is found to be more aromatic in the case of an alkyl addend.

Local aromaticity was evaluated using NICS, calculated at the geometrical ring centers for all pentagons and hexagons of each system. In Table 3, these values are given for the rings of the addition site and its surroundings, with the numbering of the rings being according to Figure 2 (NICS for the remaining rings are provided as Supporting Information; see Table S4).

When considering the substituted hydrofullerene series, little effect can be seen from the difference in functional group. The local aromatic pattern seems to be

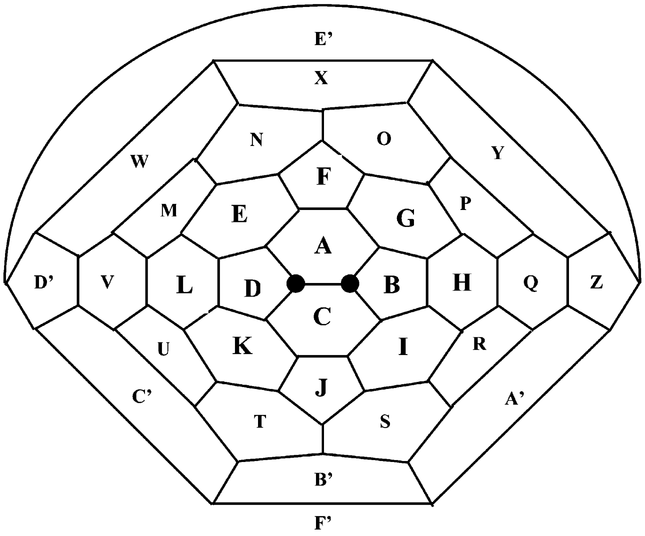


FIGURE 2. Schlegel diagram with the ring labels following a spiral rule.

little influenced by the different characters of these functional groups. This can be brought in accordance with our previous results showing the electron deficiency of the fullerene cage, together with its high global softness, to greatly influence the charge transfer between the functional group and the cage.[32] For the deprotonated systems, however, more important differences can be discerned in the vicinity of the deprotonated site.

When comparing the local aromaticity between the respective acidic and basic forms, clear differences in NICS can be seen upon deprotonation, for all the rings of the fullerene cage. The resulting negative charge is seen to cause a general reorganization of the electron density over the cage, clearly influencing the local aromatic pattern.

Also in the case of the methanofullerenes, little influence from the functional group type can be discerned in the local aromaticity, although it is more important as compared to the substituted hydrofullerenes. We note that the rings of the central pyracylenic unit, labeled A and C, can have a different NICS due to the carbene functional group facing only one of these rings.

For the methanofullerenes, the local aromatic pattern is more altered upon deprotonation in the case of the open structures as compared to their corresponding closed structures. Furthermore, the effect of the substituent R is less clear as compared to the substituted hydrofullerene series. A clear relation is seen between the NICS for the rings A and C (see Table 3) with the localization of the electrons. In case of the $C_{60}(CR^-)$ open systems, where the substituents of the type R = OR′ and NR'_2 are closer to the two rings A and C, a higher localization (more positive NICS values) is seen due to the donor character of the functional group. This effect is more important than for systems with R = H or CH_3 substituents or for the remainder of the R substituents studied, where the acceptor character of R explains the higher aromatic character of the A and C rings. Upon deprotonation of the C_{60}(CHR) structures to the $C_{60}(CR^-)$ open structures, we see that the rings labeled A and C become less aromatic in the case of R = H, OH, OCH_3, NH_2, $NHCH_3$, $N(CH_3)_2$, and CH_3 and more aromatic in case of conjugated R substituents ($CH{=}CH_2$, Ph and $C{\equiv}CH$); meanwhile, rings B and D, and F and J become more aromatic for the former group of R substituents and less aromatic for the latter group. The donor substituents thus help to localize electrons in the vicinity of the addition site of carbene. The relatively high negative values of NICS for the five-membered rings F and J can be understood as a result of a reorganization of the system: when rings A and C show a higher localization, F and J show a higher delocalization. Apart from the addition site, little difference is indeed seen for the NICS for the remainder of the fullerene (see Table S4). This clearly demonstrates the lack of interaction between the “carbene” part of the system and the fullerene cage. As was already predicted from the results in the previous parts of this section, the electron density originating from the deprotonation does not delocalize over the fullerene cage, as is, on the contrary, the case for the substituted hydrofullerenes.

IV. Conclusions

The present study of the properties of a series of substituted hydrofullerenes (C_{60}HR) and a series of methanofullerenes [C_{60}(CHR)] (R = H, OH, OCH_3, NH_2, $NHCH_3$, $N(CH_3)_2$, CH_3, $CH{=}CH_2$, Ph and $C{\equiv}CH$) has been performed and several aspects (geometric, energetic, electronic, and magnetic) were shown to be adequate for explaining the higher acidic character of the substituted hydrofullerenes with respect to the methanofullerenes series considered.

The formation of C_{60}HR systems from C_{60} is found to have a more important perturbation for the fullerene cage than the carbene addition to C_{60}, both in terms of geometrical and electronic structure. The difference in functional groups does not have an important influence, since little differences are found in geometric and magnetic properties for the groups considered.

The acidity for the methanofullerenes is predicted to be much lower as compared to the substituted hydrofullerenes. Use of their acidic properties for further functionalization will thus be less applicable for the latter series. The negative charge resulting from the deprotonation process will be more localized to the addition region in the case of the methanofullerene series, C_{60}(CHR), as compared to the substituted hydrofullerene series, C_{60}HR. The influence of the substituent is also found to be larger than for the equivalent C_{60}HR.

Analysis of the local aromatic pattern with NICS shows little influence of the functional group on the aromaticity of the system, apart from the addition site. Furthermore, the influence of the deprotonation is less important for the methanofullerenes as compared to the substituted hydrofullerenes, due to the lack of interaction between the “carbene” part of the system and the fullerene cage, further explaining their predicted lower acidity.

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Supporting Information Available: Relevant bond lengths [$d(C_1-C_2)$, $d(C_1-H)$, $d(C_2-R)$, $d(C_1-C_3)$, $d(C_2-C_3)$, and $d(C_3-R)$], the angle $C_1C_3C_2$ in case of carbene addition, and the $\Delta E(C_{60})_{def}$ at AM1 level; the electronic delocalization calculated from the Mulliken populations for all the structures calculated at the B3LYP/6-31G*//AM1 level of theory; the Mulliken charges of R, C_1, C_2, C_3, and H and the sum of the charges for the 58 nonfunctionalized carbon atoms of the cage; the NICS (ppm cgs) for the rings labeled M to F′ (See Figure 2; calculated at HF/3-21G//AM1 using the GIAO method); the optimized geometries in Cartesian coordinates of the AM1 optimizations for all structures under consideration. This material is available free of charge via the Internet at http://pubs.acs.org.

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