



Quantum calculations of acidity constants of hydro[60]fullerenes in DMSO



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ABSTRACT

The influence of the substitution pattern and chemical nature of the substituents on the pK_a values of seven hydro[60]fullerenes in DMSO was explored using quantum mechanical calculations. Two experimentally observed addition topologies with two ($RC_{60}H$) and six ($R_5C_{60}H$) substituents were considered. In the latter case, five substituents form a regular pentagram around the central pentadienyl fragment. The gas-phase free energies were calculated using DFT B3LYP and the free energies in solvent were calculated using Hartree–Fock PCM. For the substitution topologies studied, $C_{60}H_6$ had greater gas-phase basicity than $C_{60}H_2$. Differing impacts of the gas-phase and solvent free energies on the computed pK_a s were revealed and analyzed.

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The chemical products of buckminsterfullerene (C_{60}) find numerous important applications in chemistry and biology.^{1–3} An interesting feature of nanomolecules of this class is that hydrogenated fullerenes are among the strongest known organic acids.^{4–8} The strong acidity of hydro[60]fullerenes is unusual in view that compounds containing only carbon and hydrogen typically have high pK_a values.⁹ The acid–base properties of hydro[60]fullerenes are significantly affected by the pattern of chemical substitution on the fullerene cage.^{7,8} Factors controlling the pK_a of the C–H group in functionalized fullerenes are of interest for theoretical study.

The pK_a values of reactive chemical groups can be assessed by computational chemistry methods.^{10–18} The absolute pK_a values can in principle be calculated with an accuracy of 1–2 units using quantum mechanical approaches combined with a thermodynamic cycle for proton transfer in gas and solution.^{12–18} However, an earlier study of hydrogenated fullerenes using a standard continuum model overestimated the pK_a values by 10–15 units compared to the experimental data.⁸ Recently, we reparameterized the continuum solvent model specially for fullerenes and obtained realistic pK_a values of dihydro[60]fullerene and an amino acid derivative of C_{60} in different solvents.^{19,20}

The aim of the work herein was to explore, by means of quantum calculations, how the acidity of hydrogenated fullerenes

was related to molecular structure. The absolute pK_a values in DMSO for several known compounds for which acid–base reactions had previously been studied were assessed. Two important addition patterns observed in chemical reactions of fullerenes were considered. The first pattern includes the frequently utilized 1,2 addition of a functional group and hydrogen (Fig. 1). Fullerenes of the second type contain six substituents of which five functional groups are in 1,4 positions and form a pentagram around the central cyclopentadienyl moiety with an attached hydrogen (Fig. 1). Fullerenes with the pentagonal arrangement of side groups can be formed with high yields in chemical synthesis.^{1,7,8,21,22} Related molecular structures were detected experimentally,^{1–8,21,22} and a pronounced thermodynamic stabilization of these regioisomers was predicted by calculations.^{1,23}

The pK_a values were calculated from the free-energy terms in the thermodynamic cycle for proton transfer.^{13–18}

$$pK_a = (\Delta G_{\text{gas}}^* + \Delta G_s^*(A^-) + \Delta G_s^*(H^+) - \Delta G_s^*(AH)) / (2.3RT) \quad (1)$$

Here, ΔG_{gas}^* is the computed free energy of the reaction $AH \rightarrow A^- + H^+$ in the gas phase. $\Delta G_s^*(AH)$, $\Delta G_s^*(A^-)$, and $\Delta G_s^*(H^+)$ are the solvation free energies of the reactive species. * denotes a standard state of 1 mol L^{−1}. The quantum calculations for the gas phase were performed using density functional theory with the B3LYP functional.^{24,25} Molecular geometries and vibrational frequencies were calculated using the 6-31G(d) basis set, and the electronic energy term in ΔG_{gas}^* —with the 6-311++G(2d,p) basis set. Single lowest energy conformations were considered. Thermal corrections

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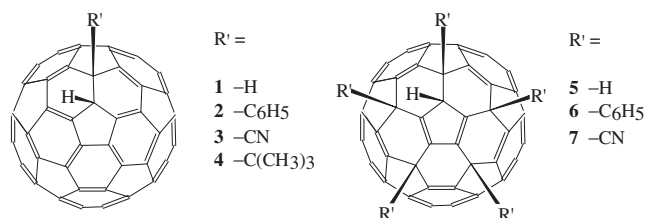


Figure 1. Chemical formulas of the molecules studied.

ΔG_{therm} for ΔG_{gas}^* were obtained by the harmonic oscillator approximation in which case the computed harmonic frequencies were scaled by a factor of 0.9806.²⁶ When appropriate, the correction for hindered rotation of the substituents was calculated using Pitzer approach.²⁷ In calculations, the free energy of a proton in gas or DMSO was -6.27^{19} and -273.3^{28} kcal mol⁻¹, respectively. The temperature of the system was 298.15 K.

The ΔG_{S}^* free energies were calculated using the polarizable continuum model (PCM).^{12,29,30} ΔG_{S}^* were calculated at the Hartree–Fock (HF) 6-31G(d) level for neutral molecules and HF/6-31+G(d) level for anions. The gas-phase optimized molecular geometries were utilized. The expression for solvation free energy in the PCM included electrostatic and non-polar contributions. The HF calculations of the polar term were performed with the integral equation formalism. The non-polar free-energy terms were obtained using analytical interatomic potentials.²⁹ The solvent cavity around molecules was built from overlapping spheres around the atom centers. The cavity radii were multiplied by a factor of 1.35 in calculations of polar contribution to ΔG_{S}^* in DMSO.³¹ All free-energy calculations were conducted using Gaussian03.³²

Atomic radii $R(X)$, which are important parameters of PCM, were calculated using the united atom scheme for HF (UAHF). The UAHF parameters take into account atom type, hybridization of atomic orbitals and bonding pattern of atom X.³⁰ Experimental data on the thermodynamics of fullerenes in solutions are very scarce which precluded direct parameterization of a solvent model for these compounds. Ad hoc use of the radii for the PCM carbon types is also not justified for buckminsterfullerene. The carbon atoms in the round-shaped molecules of fullerenes include unsatisfied π -orbitals and contain strained pyramidal arrangements of the connecting chemical bonds. The original scheme for the atomic radii in PCM does not consider such non-planar π -electron systems. To solve this problem, the PCM parameters for atoms C in neutral fullerenes and their anions were derived¹⁹ using a theoretical description of atomic hybridization and the experimental $\text{p}K_{\text{a}}$ values of reference compounds.

Firstly, the PCM expression³⁰ for the carbon radius $R(\text{C})$ was modified¹⁹ to take into account the distorted non-planar orbital hybridization of the carbons in neutral fullerene using a known approach quantifying orbital hybridization in non-planar π -electron systems.³³ The $R(\text{C})$ values were also assessed from electron density contours of $0.005 \text{ e}/a_0^3$.¹⁹ The next step of calibration employed experimental data on the relative $\text{p}K_{\text{a}}$ of 1,2-dihydro [60]fullerene **1** in toluene/DMSO.⁵ The absolute $\text{p}K_{\text{a}}$ of **1** in DMSO was linked to the measured $\Delta \text{p}K_{\text{a}}(\text{C}_{60}\text{H}_2\text{-AH})$ difference between acidities of **1** and the reference acid AH (in this case saccharin) in toluene/DMSO using a thermodynamic cycle that considered the transfer of C_{60}H_2 and AH between two solutions and alchemical transformation of C_{60}H_2 into AH.¹⁹ By virtue of formula 1 the cumulative change of $\text{p}K_{\text{a}}$ for this cycle was zero at constant temperature. In this way, the calculation of $R(\text{C})$ overall relied on certain computed free energies, and experimental data for $\Delta \text{p}K_{\text{a}}(\text{C}_{60}\text{H}_2\text{-AH})$ in toluene/DMSO and for the absolute $\text{p}K_{\text{a}}$ of AH (saccharin) and $\Delta G_{\text{S}}^*(\text{H}^+)$ in DMSO.¹⁹ The practical advantage of this

treatment is that it does not involve the unknown quantity $\Delta G_{\text{S}}^*(\text{H}^+)$ in toluene/DMSO.

The calculated geometries (ESI, Table 1) and electron structure of neutral molecules qualitatively follow the resonance valence structures presented in Figures 1 and 2a. The electron structure of the anions was more complex. Calculations demonstrated significant differences between the shapes of the highest occupied molecular orbital (HOMO) in anions of 1,2-dihydro[60]fullerene **1** and 1,2,4,11,15,30-hexahydro-[60]fullerene **5**. In C_{60}H^- , the HOMO had π -symmetry and was of a non-bonding type. This MO was spread over several atom centers (Fig. 2b). Delocalization of the HOMO in **1**⁻ reflected the possibility of multiple resonance valence structures in the corresponding Schlegel diagram of Figure 2a. In the anion $\text{C}_{60}\text{H}_5^-$, two degenerate HOMOs, containing π -symmetry and bonding type, were localized over the cyclopentadiene moiety (Fig. 2c, and d). The net negative charge was delocalized over the fullerene cage in all anions which is in agreement with earlier interpretations of the hydration phenomena for the anion Ph_5C_{60} **6**.³⁴

The computed gas-phase basicities GB for the reaction $\text{A}^- + \text{H}^+ \leftrightarrow \text{AH}$ (Table 1, ESI Table 2) were several tens of kcal mol⁻¹ lower than typical theoretical¹⁹ and experimental values for alkyl aryls. GB for hexahydro[60]fullerene **5** with a cyclopentadiene motive was 6 kcal mol⁻¹ greater than for dihydro[60]fullerene **1**. The given difference reflects the effect of the carbon cage for two substitution patterns. The GB values of hydrogenated fullerenes with the functional groups were generally lower than for reference molecules **1** and **5** (Table 1) which only contain hydrogens. The influence of the attached groups was most pronounced for molecules **6**, **7** with multiple substituents. The highest shift was found for the cyano group.

Additionally, due to the hindered rotation of bulky chemical groups for molecules **2**, **4** we calculated gas-phase free-energy corrections. The 1,2-isomers had lower energies than the 1,4-isomers in these molecules, despite the location of a H atom near the large group. The lowest harmonic frequency in the neutral fullerenes **2**, **4** and their anions corresponded to rotation of the side groups around the C–C bond that linked it with C_{60} . The free energy of the corresponding harmonic oscillator in ΔG_{therm} was replaced by the free energy of the hindered rotor. The latter term was determined from linear interpolation of tabulated data.²⁷ The B3LYP/6-31G(d)//B3LYP/6-31G(d) calculations predicted energy barriers of 5.2 and 0.4 kcal mol⁻¹ for rotation of the phenyl in **2** and **2**⁻, and 9.4 and 7.1 kcal mol⁻¹ for rotation of the *tert*-Bu in **4** and **4**⁻. In agreement with our calculations, hindered rotation of the *tert*-Bu group has been experimentally observed⁴ in **4** and the free radical **4**[•] whereas phenyl groups rotate freely in the thallium complex of **6**⁻.²² Overall, the computed corrections in

Table 1

The calculated $\text{p}K_{\text{a}}$ values and the free-energy contributions in gas phase and DMSO. Energies in kcal mol⁻¹

Entry	GB^a	$\Delta \Delta G_{\text{S}}^*(\text{A}^-/\text{AH})^b$	$\text{p}K_{\text{a}}^d$
1	310.3	–33.8	3.8
2	307.6 (–0.7) ^c	–32.9	2.4
3	302.6	–31.8	–0.5 (2.5 ⁶)
4	306.8 (0.1) ^c	–31.6	2.8 (5.7 ⁴)
5	316.3	–35.6	6.8
6	307.3	–26.1	7.3
7	279.4	–28.1	–14.7 (<–7 ⁷)

^a GB —the gas-phase basicity (additional data in ESI Table 2).

^b $\Delta \Delta G_{\text{S}}^*(\text{A}^-/\text{AH}) = \Delta G_{\text{S}}^*(\text{A}^-) - \Delta G_{\text{S}}^*(\text{AH})$.

^c The correction due to hindered rotation (in parenthesis) is included in the GB and $\text{p}K_{\text{a}}$ values.

^d The experimental $\text{p}K_{\text{a}}$ data are enclosed in parenthesis (see also ESI Table 3).

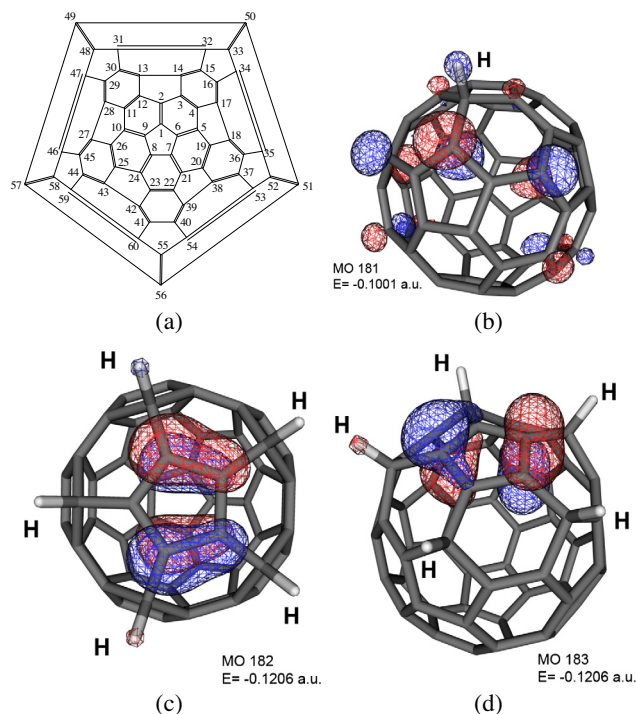


Figure 2. (a) Schlegel diagram and atom numeration¹ in C_{60} . The forms and energies of (b) HOMO in $C_{60}H^-$ and of (c) and (d) two degenerate HOMOs in $C_{60}H_5^-$. Calculations at the B3LYP/6-31G(d) level. The negative regions of orbital functions are blue and positive—red. Visualization by MOLEKEL5.4.

GB due to hindered rotor effect were found to be $-0.7 \text{ kcal mol}^{-1}$ for **2** and $0.1 \text{ kcal mol}^{-1}$ for **4** (Table 1).

The calculations showed that the pK_a s of the studied compounds were less than 8 units (Table 1, ESI Table 3). The pK_a expression 1 contains the sum of a large positive gas-phase and a large negative solvent contribution. The ranking of the $\Delta\Delta G_s^*(A^-/AH)$ values was found to be nearly opposite to the ranking of the GB values. The combined impact of the gas-phase and solvent terms led to lower pK_a values of fullerenes with functional groups **2–4**, **7** than for hydro[60]fullerenes **1** and **5**.

The calculations predicted that the acidity constant of **1** was $3.0 \text{ kcal mol}^{-1}$ greater than that of **5** (Table 1). These prototypic hydro[60]fullerenes only differ by the topology of the H atom positions on the carbon cage. The gas-phase free-energy yield was positive whereas solvent terms yielded negative contributions to the pK_a difference found in this case. It was also noted that according to calculations, dihydro[60]fullerene **1** was a slightly stronger acid than saccharine ($pK_a = 4.0$) in DMSO. The opposite had been experimentally measured in toluene/DMSO where $\Delta pK_a(C_{60}H_2-AH) = 0.6$.⁵ The pK_a shift of **1** was determined from titration curves using sodium salts of saccharine and dichloroacetic acid.⁵ In calculations, the change of relative acidities could be explained by the differences in $\Delta\Delta G_s^*(A^-/AH) = \Delta G_s^*(A^-) - \Delta G_s^*(AH)$ for **1** and saccharine upon transfer between two solvents.

Combined experimental data in two solvents had showed that *tert*-Bu-hydro[60]fullerene **4** should be a weaker acid than dihydro[60]fullerene **1**.^{4–6} A value of $pK_a = 5.7$ was determined for **4** by titration using reference acids saccharin ($pK_a = 4.0$), 2,4-dinitrophenol ($pK_a = 5.1$), and dichloroacetic acid ($pK_a = 6.4$) in DMSO.⁴ In our calculations, the pK_a value for *tert*-Bu $C_{60}H$ was 1 kcal mol^{-1} lower than for $C_{60}H_2$. Such a result mainly stems from the lower GB value for **4**, while solvent terms favored a greater acidity of **1** (Table 1). It can be noted that an even greater negative difference ($-2.5 \text{ kcal mol}^{-1}$) between the pK_a s of compounds **4** and **1** was predicted in earlier calculations⁸ using a standard PCM.

The acidity of another important molecule $PhC_{60}H$ **2** was found to be lower than that of *tert*-Bu $C_{60}H$ **4**. However, when molecule **6** with five phenyl substituents was considered, a substantial decrease of anion stabilization in solution led to **6** having a higher pK_a than **1**, **2**, and **5** (Table 1). The lowest pK_a values in the considered series were found for hydro[60]fullerenes **3** and **7** containing cyano groups. These compounds also have the lowest experimental pK_a s. The computed pK_a s were underestimated for these compounds by several units. The discrepancy found can probably, as in case of **4**, be explained by the insufficient accuracy of the gas-phase results. In particular, use of high-level methods is essential for accurate prediction of gas-phase basicity of molecules with the cyano group.³⁵ It is well known that the importance of the accuracy of gas-phase data cannot be underestimated for pK_a calculations.^{12–18} The high-end calculations of functionalized fullerenes, however, meet clear technical limitations due to the large number of atoms in the systems studied. It can also be noted that pK_a calculations using DFT B3LYP at a comparable theory level also gave uncertainties of $1–2 \text{ kcal mol}^{-1}$ for small molecules.^{15,16}

In this work, we have attempted to separate and analyze the effects on pK_a of the topological position of reactive hydrogen in hydro[60]fullerenes and of the chemical nature of substituents in solvent. The calculated pK_a s of compounds **1–7** via Eq. 1 were determined to be less than 8 pK_a units. The ranking of the cumulative solvent terms in ΔG_s^* was found to be nearly opposite to the ranking of the gas-phase free energies for the molecules considered (Table 1). The calculations showed that 1,2 addition of two hydrogen atoms to buckminsterfullerene yields a more acidic product than 1,2,4,11,15,30 addition of six hydrogen atoms. Such a difference between solution pK_a s is mainly due to the thermodynamically less favorable deprotonation of **5** in the gas phase which reflects the intrinsic effect of the carbon cage for the considered substitution patterns. The calculated pK_a values only qualitatively follow Hammett's constants for side groups.³⁶ The hydro[60]fullerenes with the CN substituents— $CNC_{60}H$ and $CN_5C_{60}H$, were found to be the strongest acids among the molecules studied which is mainly due to the predominant effect of the gas-phase contribution. The hindered rotor correction to the gas-phase free energies cannot be neglected in some cases. The pentadienyl hydro[60]fullerene containing five aromatic groups $Ph_5C_{60}H$ was the weakest acid among those considered which can be explained by an unfavourable balance of solute–solvent interactions.

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Supplementary data

Supplementary data (optimized geometries of the neutral molecules and anions **1**, **5** and the free energy terms in gas phase and DMSO of compounds **1–7**) associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.tetlet.2015.09.049>.

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