Calculations of PAH anions: When are diffuse functions necessary?†

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The effect of including *vs.* excluding diffuse functions while calculating numerous parameters of PAH anions by various calculation methods is discussed. The omission of diffuse functions appears to have a negligible effect while calculating geometry parameters or total energy; thus, acceptable results may be obtained without them. The conclusions for charge density appear to be the same; however, limited results make an unambiguous claim unachievable. Calculating ^{1}H- and ^{13}C-NMR shifts undoubtedly requires the use of these functions.

Introduction

For some time now, computational chemistry has been an important tool for probing, observing, explaining and verifying what had been discovered experimentally.[2] Calculations may verify or refute results still in question, or explain chemical, physical and other phenomena, whilst discovering previously unknown trends. Combining experiment and theory results in a powerful and efficient instrument, enabling study of any kind of chemistry. Theoretical chemistry, therefore, is an important tool, having a critical position as a companion to experimental results, playing a significant role in the advancement and development of today's chemistry in general, and the research in polycyclic aromatic hydrocarbon (PAH) anions, in particular.

In this paper we are concerned with the necessity of diffuse functions in the calculation of large conjugated anions, especially PAH anions. PAH anions have also been the focus of extensive research, as they exhibit extraordinary properties, pertaining to key questions of much interest in organic chemistry.[3–6] The study of PAH anions is widespread, particularly in organic chemistry as they are models for charged graphite, fullerenes and other carbon-based compounds. Additionally, interest in PAHs and their anions ranges from synthetic,[7] medicinal and biological[8] chemistry, to environmental[9] and interstellar[10] chemistry. Theoretical characterization of PAHs and their anions is therefore critical to understanding their reactivity.

The heart of straightforward calculations is the proper choice of basis sets. Improvement of a calculation, in order to obtain more reliable and accurate results, closer to experimental values, is possible *via* a change in the calculation protocol. For instance, one may use an extended basis set, utilizing three or more lobes to describe an orbital; or employ polarization functions,[11] describing the change imposed on an orbital during the transition from free to bonded state.

Diffuse functions constitute a further effort to improve theory. Just as the insertion of extra electrons into orbitals brings about their natural growth in order to reduce the Coulomb repulsion, so must a theoretical calculation allow for expression of such a change. Development of diffuse functions allowed orbital flexibility during calculation, allowing a more accurate description of the true, diminished electron repulsion, mainly for anions, and lowering the estimate of total energy, in accordance with the variation principle.[12]

The use of diffuse functions originated from the calculation of atomic anions, such as for H^-, F^-, Li^- and O^-.[13] The investigation of such anions demonstrated that without diffuse functions, even stable anions, such as O^-, Cl^- and F^- are calculated to be unstable.[14] Calculating anions without diffuse functions generally overestimates mutual electron repulsion,[13] and even gives false interactions of each electron with itself.[15] Various small anions have been shown to commonly need diffuse functions for useful calculations.[13] Moreover, it has been shown that standard basis sets using *only one* set of diffuse functions for calculating properties of small anions may give inadequate results, indicating the necessity for double-diffuse functions.[16] It is important to note that in *all* these cases, assumptions regarding the necessity of diffuse functions were based on calculations of anions with *point* charges. In such cases, the charge is almost entirely located on a *single* atom.

These and other[17] difficulties lead to the supposition that standard calculations are not appropriate for negative atomic and molecular anions, and eventually resulted in the inclusion of diffuse functions as a general prerequisite for reliable anionic calculations. This pertained to small molecular anions, as well as to atomic anions. Duke's work[18] on the methyl anion showed that the inclusion of diffuse functions proved to be critical for adequate representation of the anion. Even relatively small basis sets including diffuse functions, such as 3-21+G, were found to describe the geometries and proton affinities of small molecular anions, such as BeH^-, BH_2^-, NH_2^- and OH^-, fairly accurately.[13] While calculating equilibrium geometries, the inversion barrier and other properties of CH_3^- and CH_3 using *ab initio* methods, Driessler showed[19] that SCF values obtained using diffuse functions were substantially more accurate than previous results calculated without them. Driessler's results reinforced Duke's,[18] also showing that, lacking diffuse functions, one obtains positive orbital energy for the highest occupied orbitals for negative anions. Davidson and Schaefer both independently confirmed this later on.[20]

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The necessity of diffuse functions in calculations and their contribution to various properties have been widely studied.[21–26a–c] The importance of diffuse functions has been investigated with respect to polarizibility and dipole and quadruple moments,[21a–c] relative,[22a] binding[22b,c] and reaction[21c,22d] energies, as well as electronic interactions.[23] The effect of diffuse functions on vibrational frequencies,[22b] electron transfer,[24] hyperfine splitting constants[25] and conformational energy[22d] has also been studied. The necessity of diffuse functions for calculating electron affinity has especially been examined.[21a,22b,24–26] The relation between geometry and diffuse functions has also been analyzed,[21c,22b,25,26a] although mostly for small and specific families of compounds. Generally speaking, in almost all cases, the introduction of diffuse functions into the calculation improved calculation results substantially.

However, while the use of larger and/or more complex basis sets usually yields more accurate results, this is almost always accompanied by a significant increase in calculation effort and time. This is *particularly* evident for large molecules, such as PAHs. A calculation with diffuse functions for PAHs is difficult and often quite impractical, since these large molecules may contain a sizeable number of atoms. Such calculations require augmented computational resources, calculation times can be larger by a full order of magnitude, and failures in convergence are common. At the same time, the actual necessity of diffuse functions for these types of molecules can be questioned. The distribution of charge over a large spatial area reduces inter-electron repulsion. Additionally, charged PAHs may exhibit enhanced delocalization of π-electrons, for through this method, they attain aromatic stability. Thus, an examination of the actual contribution and necessity of diffuse functions for several specific cases has been undertaken.

Is it possible that through size and delocalization PAH anions reduce inter-electron repulsion to such a degree that the use of diffuse functions is not necessary to accurately describe the system? At the present time, the few DFT calculations performed on PAH anions have not extensively examined all parameters in this work.[26,27] In this paper, we present calculated results regarding the above question.

Computational details

All computations were carried out using the GAUSSIAN '98 program package,[28] with the exception of NBO analyses,[29] which employed JAGUAR 4.0 software.[30] All calculations of molecule parameters were carried out at a DFT level employing Becke's three-parameter hybrid density functional with the non-local correlation functional of Lee, Yang and Parr (B3LYP),[31,32] and with Hartree–Fock methods. Four different basis sets were used: 6-31G*, 6-31+G*, 6-311G** and 6-311+G**;[33,34] thus, each molecule was calculated with a total of eight different methods. All structures calculated were geometrically optimized within their highest symmetry point groups, and harmonic vibrational frequencies were computed to confirm that the stationary points correspond to minima. Only minimum energy structures were considered for NMR and NBO calculations. NMR chemical shifts were derived from additional single point calculations employing the GIAO[35] method as implemented in GAUSSIAN '98. The isotropy values obtained in this way were subtracted from the respective isotropy values obtained for optimized TMS[36] (see ESI)† in order to obtain NMR chemical shifts.

Methodology

Primary parameters evaluated in this work are geometry (bond lengths and intramolecular angles), total energy, ^{1}H- and ^{13}C-NMR chemical shifts and charge density (on carbons and protons, though the density on carbons are of main interest). While other properties, some more sensitive to diffuse functions, such as electron affinities, dipole moments and polarizabilities could also be examined, we nevertheless chose to focus on parameters central to PAH anion research generally, and particularly to systems previously studied in our laboratory.[37] Various aspects, such as size, conjugation ability, charge states and systems with or without five- and six-membered rings were sampled.

For these goals, calculations were made on a large series of different anions (mostly PAHs), namely, methyl (**1**), ethyl (**2**), *n*-propyl (**3**), iso-propyl (**4**), *n*-butyl (**5**), *tert*-butyl (**6**), formate (**7**), acetate (**8**), indenyl (**9**), fluorenyl (**10**) and cyclopentadienyl (**11**) anions (Scheme 1); and the acenaphthalene (**12**), pentalene (**13**), pyracylene (**14**), pyrene (**15**), phenanthrene (**16**), anthracene (**17**), tetracene (**18**), fluoranthene (**19**), indenofluoranthene (**20**), and cyclooctatetraene (**21**) dianions (Scheme 2). Various comparisons were made in order to determine the effect of the use of diffuse functions on the different parameters calculated.

Results and discussion

Taking indenyl anion (**9** and Scheme 3) as a general example, the results arising from calculations with diffuse functions are practically identical to those arising from calculations without these functions.[38] The comparisons typically performed weigh parameters for the four calculations performed with diffuse functions (HF/6-31+G*, HF/6-311+G**, B3LYP/6-31+G*, B3LYP/6-311+G**) against the analogous ones without them. The largest difference relating to the molecular bond lengths, between results arising from the HF/6-31+G* calculation and those acquired from using the HF/6-31G* method is only 0.004 Å.[38] This corresponds to only 0.28% of the respective bond length.[39] For all other comparisons (*i.e.* between other basis sets and calculation methods), the difference is at most the same value. The largest difference in intramolecular angles (between the same two calculation methods and basis sets) was 0.194°, 0.15% of the respective angle. Only the difference between B3LYP/6-31+G* calculated values and those obtained from B3LYP/6-31G* is larger; 0.202°, also 0.15% of its respective angle. Examining the calculated total energy, one finds similar results: ΔE is 0.032 au between B3LYP/6-31+G* and B3LYP/6-31G*, and smaller still for all other three comparisons.

In comparison, the differences relating to charge densities and particularly to NMR shifts were somewhat larger. The largest difference relating to charge density on carbons was 0.02 charge units (HF/6-31+G* *vs.* HF/6-31G*), equaling a 7.63% difference of charge density on the corresponding carbon atom. The largest differences for NMR shifts were 7.60 ppm for carbons (B3LYP/6-31+G* *vs.* B3LYP/6-31G*), and 0.70 ppm for protons (HF/6-311+G** *vs.* HF/6-311G**).[40]

On the whole, most differences appear to be quite small, sometimes exceptionally so, to a point where they are
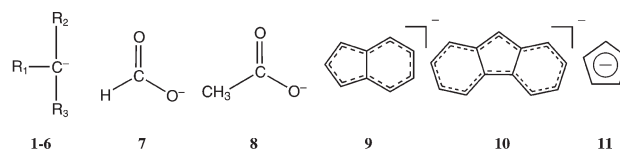
1: R$_1$ = R$_2$ = R$_3$ = H
2: R$_1$ = Me, R$_2$ = R$_3$ = H
3: R$_1$ = Et, R$_2$ = R$_3$ = H
4: R$_1$ = R$_2$ = Me, R$_3$ = H
5: R$_1$ = n-Pr, R$_2$ = R$_3$ = H
6: R$_1$ = R$_2$ = R$_3$ = Me

**Scheme 1** Monoanionic systems studied in the present work.
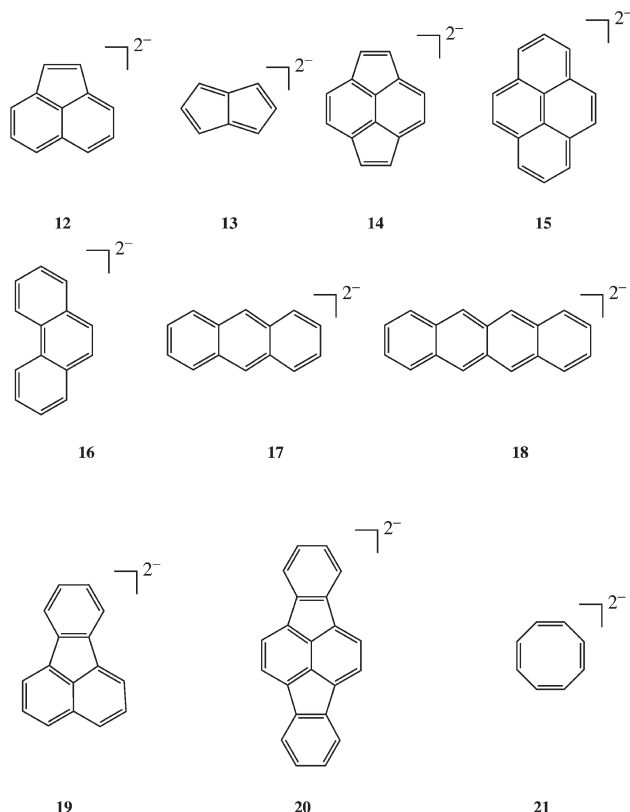
Scheme 2 Dianionic systems studied in the present work.

insignificant. As we shall see, this appears to be the case in most instances for calculated PAH anions in the present work.

Geometry

By comparing the basis sets 6-31G* with 6-31+G* and 6-311G** with 6-311+G** for HF and B3LYP separately, and by plotting the maximum differences for each parameter against the number of atoms in the skeleton,[41] one can obtain four different figures for each calculated parameter. Fig. 1 shows that the comparison between the B3LYP/6-311G** and 6-311+G** calculations,[42] methods that differ only by a single diffuse function, show highly different behavior for four different types of anions. Anions derived from regular saturated alkanes, such as the methyl and ethyl anions, have a fairly large difference for Δr_{max}. Thus, without the use of diffuse functions, calculated geometries of small anionic molecules with significant charge density show considerable errors, reinforcing Duke[18] and Driessler's[19] results. *n*-Propyl (**3**) and *n*-butyl (**5**) behave similarly. However, the alteration
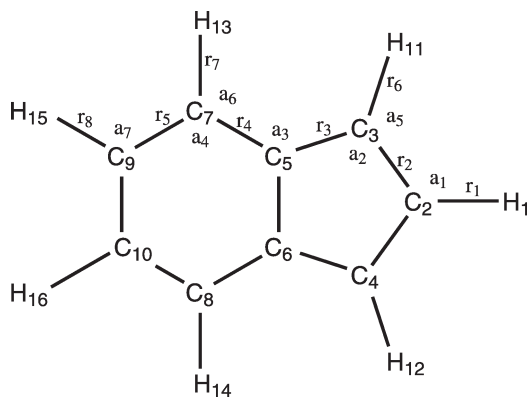
Scheme 3 Defined parameters for the indenyl anion (**9**).

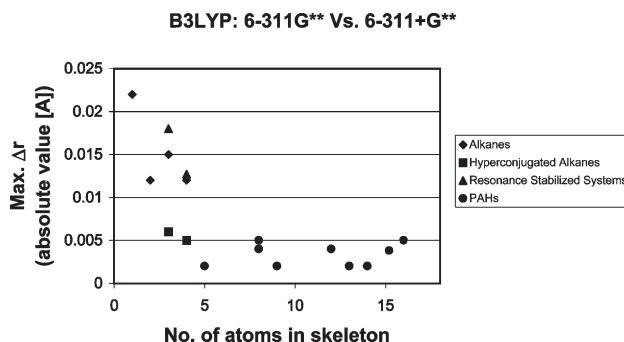**Fig. 1** Correlations between anion skeletal size and the absolute maximum difference in bond length, Δr_{max}, between B3LYP/6-311G** and B3LYP/6-311+G** calculated values.

of these anions to iso-propyl (**4**) and *tert*-butyl (**6**) give rise to a considerable reduction in Δr_{max}. The average figures are approximately three-fold smaller than those for their *n*-alkyl analogues. The difference in connectivity of these sets of molecules is apparently significant to their stability. The ability for hyperconjugation in these anions apparently disperses the charge in a much more effective way than in the *n*-alkyl anions; thus, the effect of diffuse functions in the calculation becomes less noticeable. It is important to note that comparisons for all other three pairs of basis sets show similar results.

The two models for resonance-stablized anions in this study, formate and acetate, indeed both show a much smaller Δr_{max} than for *n*-alkyls, even ones with the same number of atoms in their skeleton. It can be rationalized that the negative charge is much less localized in these resonance-stabled anions compared with those of the *n*-alkyls, where the charge resembles more of a point charge. Bond lengths in resonance stabilized molecules are therefore less susceptible to changes due to extra charge compared with *n*-alkyls, and parameters calculated with functions taking this charge into consideration are therefore less likely to be significantly different from those calculated without these functions.

For cyclopentadienyl anion (**11**) and cyclooctatetraene dianions[43] (**21**), Δr_{max} drops off even further. For the PAHs, Δr_{max} is of the same order. This is understandable, as most PAHs discussed here contain both aromatic stabilization (similar to the resonance stability of formate (**7**) and acetate (**8**) anions) *and* a large number of atoms in their skeleton. The order of magnitude of maximum bond length difference obtained for the indenyl anion, the smallest PAH studied, is already extremely small, and repeats itself for almost all other PAHs whose geometrical values were calculated in this work.

The only anomaly appears to be for the calculated differences of tetracene dianion (**18**), between 6-311G** and 6-311+G** in the Hartree–Fock method.[38] This may be due to the known fact that bond lengths in neutral tetracene deviate largely from each other: the longest bond being 1.452 Å, the shortest, 1.367 Å.[44] Bond lengths at the central ring of phenanthrene show similar magnitudes of Δr. Structural criteria are important in defining aromatic molecules.[45] Nevertheless, neither the aromaticity of tetracene nor that of phenanthrene[46] is questioned, and in any case, this aberration does not recur for the other parameters calculated for tetracene.

Intramolecular angles show the same trend as that seen for bond lengths. Fig. 2 shows that the comparison between B3LYP/6-311G** and 6-311+G** methods. While methyl anion has an average $\Delta\alpha_{max}$ of about eight degrees, and the rest of the alkyls an average $\Delta\alpha_{max}$ of ~4–5, there is a decline in these figures when moving to the iso-alkyl anions (*ca.* 0.7–1.4°) and furthermore when proceeding to the resonance-stabilized anions of formate (**7**) and acetate (**8**) (*ca.* 0.57 a degree and less). This interesting decline continues for the PAH anions, as no difference is greater than 0.43°. The acetate
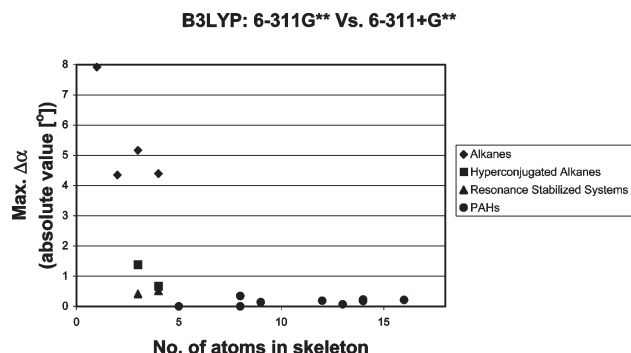
B3LYP: 6-311G** Vs. 6-311+G**

Fig. 2 Correlation between anion skeletal size and the absolute maximum difference in intramolecular angles, $\Delta\alpha_{max}$, between B3LYP/6-311G** and B3LYP/6-311+G** calculated values.

anion, containing only 4 atoms in its skeleton, shows a difference only slightly larger than that of pentalene dianion (**13**), the PAH with the largest $\Delta\alpha_{max}$. After reaching a minimal aromatic[41b] hydrocarbon size (*ca*. 5 carbons) the introduction of additional carbons into the skeleton or even additional rings, does not appear to have much effect on the difference, as long as conjugation remains possible. Similar conclusions to the fact that calculated geometry related parameters of PAH anions are not affected greatly by the addition of diffuse functions have been achieved before, most recently by Schaefer and Schleyer,[26a] although these conclusions have been made for smaller and more specific families of PAH anions. Comparisons for all other pairs of basis sets showed similar results.[38]

No such correlations were found (for either bond lengths or intramolecular angles or any of the other parameters discussed in this work) when attempting to associate the differences with other factors, such as the total number of rings, the number of five-membered rings, or the ratio between the number of carbons to the number of rings.

Energy

Energy is a clear case in which one *cannot* compare the absolute differences, as total energy varies *considerably* from molecule to molecule, *especially* when moving from small anions to PAHs, which have a very large number of wavefunctions.[47] Using the B3LYP/6-311G** and B3LYP/6-311+G** methods, for instance, one calculates -39.829 au and -39.856 au for the methyl anion (**1**), respectively. The much larger hyperconjugated *tert*-butyl anion (**6**) has energies of -157.809 au and -157.836 au, calculated by the above two methods, respectively. Lastly, the even larger PAH fluoranthene dianion (**19**) has energies of -615.775 au and -615.802 au, respectively.[38] The difference between the two calculation methods for all three molecules comes to approximately 0.027 au. However, one realizes immediately that this difference of 0.027 au does not carry the same significance for each anion. One cannot compare a difference of 0.027 au out of approximately -40 au with the same difference out of roughly -615 au. Therefore, in this case, the figures shown are those for *relative* ΔE *vs.* the number of atoms in the skeleton.

Fig. 3 depicts the differences arising from the comparison between B3LYP/6-311G** and 6-311+G** methods. As for geometry, comparable trends are found for all comparisons[38] pertaining to ΔE as well. It is important to note that unlike in the gas phase, where electrons of highly charged anions are considered to be unbound, in *all* calculations in this work, the electrons are restricted to be attached to the skeleton of the molecule. Effectively, this means that values obtained here (regardless of basis set used *and* the existence of diffuse functions), only result in an *estimate* for the ground-state energy. In other words, the values should most probably only
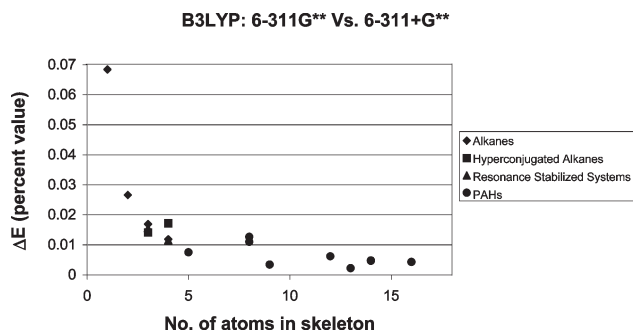
B3LYP: 6-311G** Vs. 6-311+G**

Fig. 3 Correlation between anion skeletal size and the relative difference in total energy, ΔE, between B3LYP/6-311G** and B3LYP/6-311+G** calculated values.

be considered *qualitatively*. In this regard, and with respect to the historical difficulties reported,[18–20] it is highly important to note that *all* total energies for PAHs turn out to be negative, as expected from experiment.

While most studies in the past concluded that diffuse functions are critical to the improvement of calculated energies,[22b–d] these were based on knowledge mainly from *atomic* anions. For PAHs, we conclude that the use of diffuse functions for calculating total energy improves the energy by only *ca*. 0.01% or less. These trends are in good agreement with conclusions reached by Schleyer and Schaefer for the more specific family of cyclopentadiene-annulated PAHs.[26a]

NMR shifts

One of the main objectives of this work was to deduce conclusions regarding NMR shifts, as this is of utter importance and a main tool in examining aromaticity and aromatic-related properties in charged PAHs.[48] Specifically, ^{13}C-NMR shifts are of more interest to our study, as these shifts show an empirical correlation between the additional charge each carbon obtains upon reduction and the shift change of each carbon introduced due to charging of the molecule. NMR shifts, therefore, show clear relationships to various important parameters, such as charge distribution, anisotropy, aromaticity,[49a,50] anti-aromaticity,[49b–e,50] the HOMO–LUMO energy gap and paramagnetism,[49b–e] and are of major importance to organic and theoretical chemists.

Fig. 4 shows the maximum differences, $\Delta\delta_{C\ max}$, between B3LYP/6-311G** and 6-311+G** methods *vs.* the number of atoms in the skeleton.[41b,51] Here, the difference must be viewed as the absolute difference, as NMR shifts (relative to TMS) may differ *considerably* from solvent to solvent, and the choice of solvent is arbitrary. Furthermore, the choice of TMS as a standard is arbitrary as well. The above is *especially* true for ^{13}C-NMR, where the typical field is much larger;

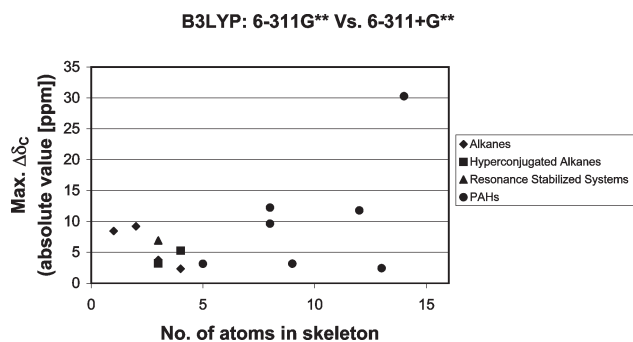**B3LYP: 6-311G** Vs. 6-311+G****

Fig. 4 Correlation between anion skeletal size and the absolute maximum difference in ^{13}C-NMR shifts, $\Delta\delta_{C\ max}$, between B3LYP/6-311G** and B3LYP/6-311+G** calculated values.

aromatic carbons typically resonate at 110–150 ppm, while aliphatic ones show resonances mainly in the 10–30 ppm region. While PAH anions generally produce a difference of 12 ppm or smaller, the differences for the small alkyl anions are less, and PAH anions give differences often larger than those calculated for the *n*-alkyl or iso-alkyl carbanions.[38] $\Delta\delta_{C\ max}$ values typically in the order of 10 ppm surely are not negligible. Calculations utilizing B3LYP methods accentuate this fact.[38] These findings are as expected, and agree with those of Jaszuński *et al.*[52] that the use of diffuse functions for NMR shieldings are less important; larger basis sets with more flexible core functions should be employed. Anthracene dianion (**17**) shows the largest difference, over 30 ppm in the 6-311G** *vs.* 6-311+G** comparison in the B3LYP method. This relatively large difference is an irregularity and is discussed later. In any case, this difference for the anthracene dianion (**17**) is *far* smaller in the other comparisons made.[38] With respect to $\Delta\delta_{C\ max}$, there is no apparent decline in value in advancing from small aliphatic anions to π-conjugated systems.

Since the only physical parameter easily obtainable for comparison with calculated data is NMR shifts, evaluation of these experimental values with respect to those calculated is obviously called for and necessary. Fig. 5 shows examples of correlations between experimental[53] ^{13}C-NMR values, and those calculated in this work with and without diffuse functions, for various PAH dianions. While fairly small dissimilarities exist between the three graphs in each figure, the overall picture is clear: while some significant differences between calculated data with, and without, diffuse functions do occur, the *pattern* is replicated fairly well. The square of the correlation factor between these two sets of data[54] is 0.965 for the acenaphthalene dianion (**12**), and even higher values for R^2, of 0.999, 0.999 and 0.992 are obtained for the same comparison for the anions of fluorene (**10**), indene (**9**) and pyracylene (**14**),[38,54] respectively. R^2 is largely of the same order of magnitude for comparisons between calculated data (either with diffuse functions or without) and experimental values. R^2 is often even better for comparisons between experimental values and calculations made without diffuse functions than with calculations employing these functions.[38] This information clearly shows that while diffuse functions are essential in calculating ^{13}C-NMR shifts, calculated NMR

shifts without diffuse functions may provide for assistance in experimental assigning.[48c]

^{1}H-NMR shifts show similar behavior with relation to the effect of diffuse functions. Fig. 6 shows the $\Delta\delta_{H\ max}$ difference between B3LYP/6-311G** and 6-311+G** calculated methods.[41b,51] $\Delta\delta_{H\ max}$ is frequently on the order of 1 ppm or more. This is even a more critical error than for $\Delta\delta_{C\ max}$. Here, too, $\Delta\delta_{H\ max}$ for PAH anions and other, non-aromatic anions seem to be on the same order of magnitude, again agreeing with the results of Jaszuński *et al.*[52]

This trend, which appears to be a major distinction from the other figures in general and from $\Delta\delta_{C\ max}$ in particular, presumably reflects the fact that peripheral protons' NMR resonances are affected in a crucial way by anisotropic effects. This is in sharp contrast to peripheral carbons, which are insensitive to anisotropic effects.[55]

These anisotropic effects may possibly explain the anomaly in anthracene, which, as well as many linear acenes, is customarily regarded as less stable than its angular counterpart.[56] Randić suggested[57] that this is due to a smaller number of $(4n+2)$ π-electron conjugated circuits possible in such species. The linear systems cause significant dilution of the aromatic sextet.[56a] Schleyer proposed[58a] that anthracene has only one resonant sextet located in the central ring. The NICS value for this ring is significantly larger than that of benzene; conversely, NICS values for the outer two rings are smaller than that of benzene.[58] The works of Ligabue *et al.*[59] concerning density maps of anthracene, phenanthrene and triphenylene; and later on, of Ruiz-Morales[60] on HOMO–LUMO gaps of PAHs, further supported Schleyer's conclusions.

All of the above bring support to the fact that anthracene and anthracene dianion (**17**) may contain significant anisotropic effects.[49b–e] Thus, ^{1}H-NMR shifts are most affected and, as mentioned above, slightly less for ^{13}C-NMR. Non-magnetic related parameters, such as geometry (and energy to some extent), are hardly affected.

Comparison to experimental[38,54,61] ^{1}H-NMR values (Fig. 7) gives rise to a similar image. While R^2 between a specific calculated data (either with diffuse functions or without) and experimental values varies from poor (indenyl, **9**) through fair (acenaphthalenyl, **12**) to quite good (fluorenyl, **10**),[62] correlation factors between calculated data obtained with,
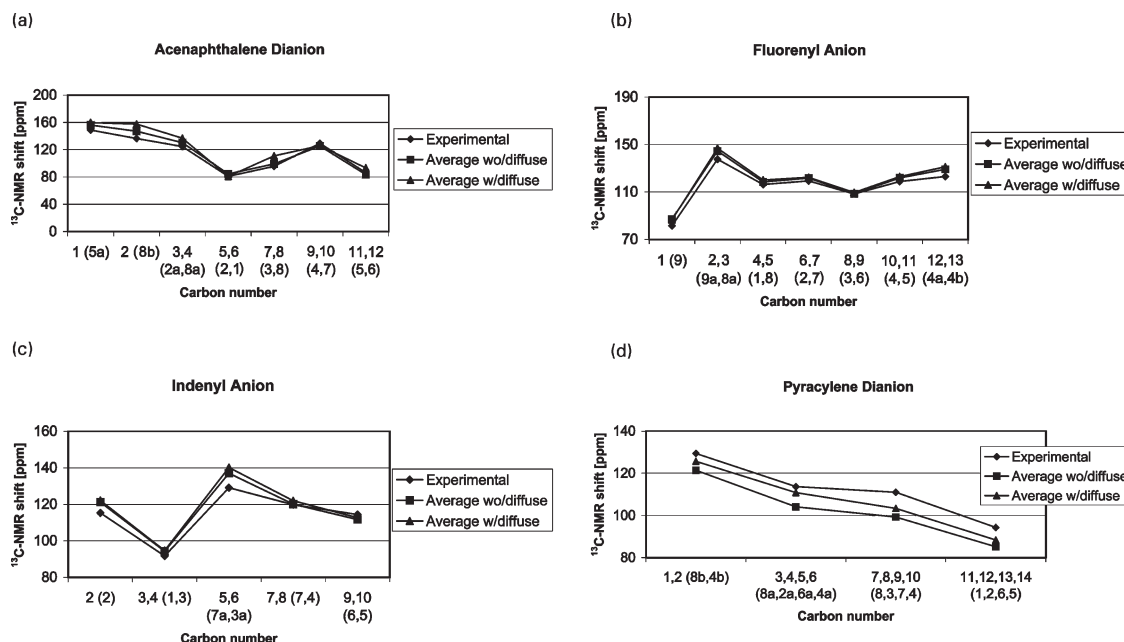
Fig. 5 Correlations between calculated ^{13}C-NMR shifts (with and without diffuse functions) and experimental values. IUPAC numbering in parentheses.[68] Acenaphthalene dianion, (a); fluorenyl anion, (b); indenyl anion, (c); pyracylene dianion, (d).
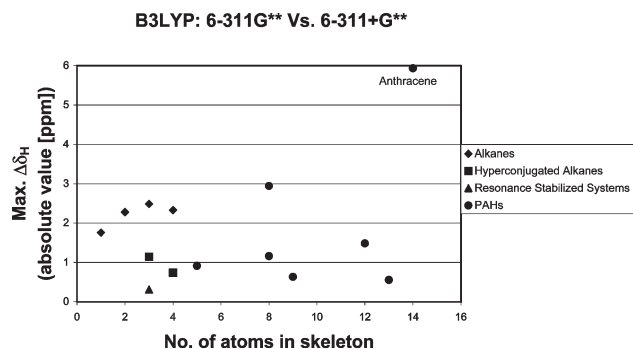
Fig. 6 Correlation between anion skeletal size and the absolute maximum difference in ^{1}H-NMR shifts, $\Delta\delta_{H\ max}$, between B3LYP/6-311G** and B3LYP/6-311+G** calculated values.

and without, diffuse functions are good throughout. R^2 between these two sets of data is 0.985 for the acenaphthalene dianion (**12**) and 0.995 and 0.981 for the anions of fluorene (**10**) and indene (**9**), respectively.[63] This further supports the supposition that although diffuse functions are critical in calculating ^{1}H-NMR shifts, if calculation is meant only to assist in assignment, then one may possibly do so from calculated data excluding diffuse functions.

Charge density

For charge density, the trends exhibited for geometry and energy are reiterated. Fig. 8 shows $\Delta\rho_{max}$ for the B3LYP/

(a)

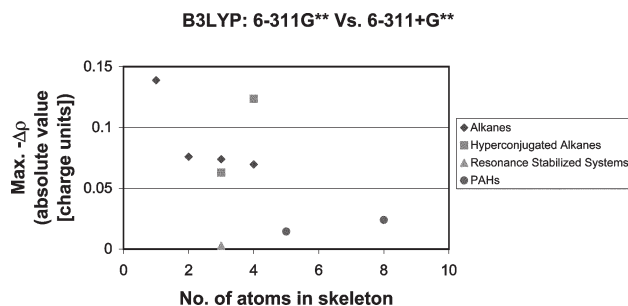

(b)

(c)

Fig. 7 Correlations between calculated ^{1}H-NMR shifts (with and without diffuse functions) and experimental values. IUPAC numbering in parentheses.[68] Acenaphthalene dianion (a); fluorenyl anion (b); indenyl anion (c).

Fig. 8 Correlation between anion skeletal size and the absolute maximum difference in charge density, $\Delta\rho_{max}$, between B3LYP/6-311G** and B3LYP/6-311+G** calculated values.

6-311G** and 6-311+G** comparison.[41b,51,64,65] As in the previous cases mentioned, also here one can see the distinction between the π-conjugated system/PAH region and the alkyl anion region. Even the smaller PAHs have relatively smaller $\Delta\rho_{max}$ than the alkyl anions. Similar trends are found for all other comparisons.[38]

However, since far fewer points appear on these graphs than on the corresponding ones for geometry and energy,[51,64] one should be cautious when drawing conclusions. At any rate, NBO calculations apparently confirm the underlying working assumption; PAHs have a much smaller density of charge within their carbon-skeleton framework.

Scheme 4 graphically shows that PAHs have a far less density of charge in their carbon skeleton due to their far larger size and π-conjugation ability. These findings clearly indicate that the contribution of diffuse functions to the calculation of charge density in PAH anions would be quite small. This contrasts the conclusions concerning small anions, as in the investigation of the hydride ion by Shore et al., who showed[66] that without diffuse functions, the local exchange approximation of the ground state failed, giving an incorrect ground state, with partial delocalization of the electrons. Therefore, one can, albeit vigilantly as mentioned above, conclude that the inclusion of diffuse functions in calculations of charge density does not cause the results obtained without them to change significantly.

General

From looking at all figures and data,[38] one can see some general trends common to all cases:

(i) For almost all parameters calculated, the difference between larger basis sets (6-311G** and 6-311+G**) is less significant than the difference between smaller ones (6-31G* and 6-31+G*). This is understandable, as larger basis sets allow more flexibility in the calculation; consequently, allowing further flexibility using diffuse functions is of less importance in these cases. When charge delocalization is present, inter-electronic repulsion is already being dealt with by larger basis sets and polarization functions. The exception to this case is NMR differences: in these instances the differences follow no specific trend.
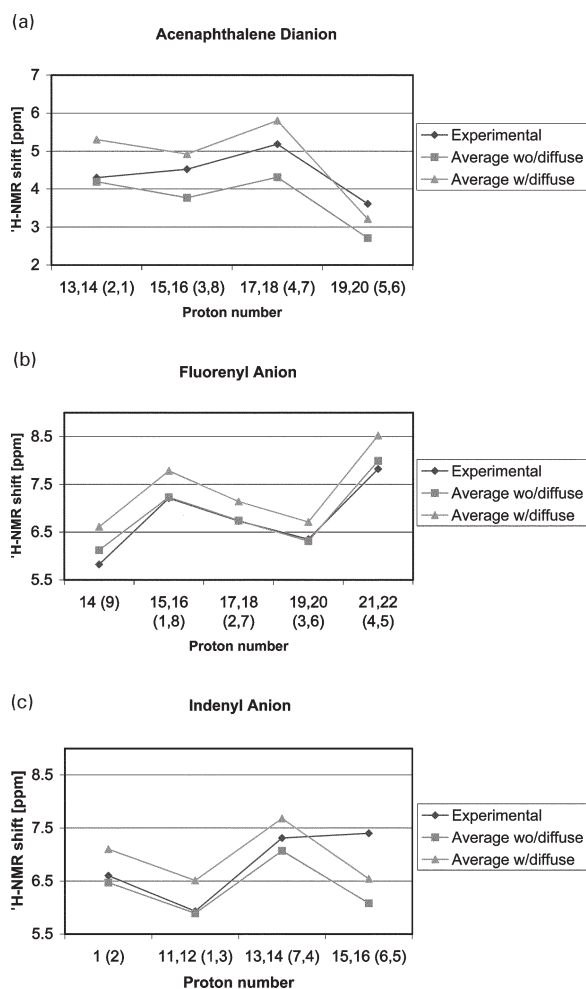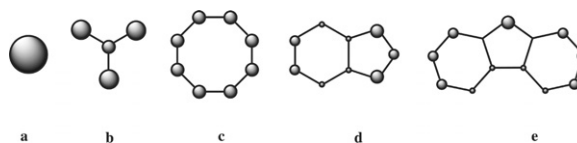
Scheme 4 Charge density for various anions, as calculated from NBO (B3LYP/6-311G** results). All spheres represent negative charge. Size of sphere represents charge, relative to 100% as depicted for the methyl anion. Methyl anion (a); tert-butyl anion (b); cyclooctatetraene dianion (c); indenyl anion (d); fluorenyl anion (e).

(ii) Generally, *n*-alkyl and iso-alkyl anions exhibit the property that differences between two basis sets are larger for a B3LYP calculation than for the analogous calculations using HF theory. This is in harmony with Truhlar's results[22d] on alkyls and other relatively small molecules. Diffuse functions appear to be of much more significance for DFT than for Hartree–Fock in these cases.

For PAHs, however, these differences are, on the whole, much smaller. In fact, the differences between two B3LYP calculations are almost identical to those obtained from the same basis sets in HF. For a sizeable number of occurrences, the difference is actually smaller for B3LYP calculations than for those calculated in the HF method.

(iii) Since the differences reported are absolute values, it is noteworthy to examine trends within the differences (not only the maximum differences). It should be pointed out at the start that all trends reported now are essentially the same regardless of the difference in basis sets or calculation methods.

The addition of diffuse functions does not appear to result in a trend concerning the sign of the difference, *i.e.* calculations including diffuse functions give larger values than calculations excluding them roughly the amount of instances than *vice versa*. In the specific case of Δr, PAH anions show a slight leaning towards *negative* differences, *i.e.* larger values for results obtained *without* diffuse functions than those obtained with them. In energy calculations, more than 95% of the cases show a negative difference for ΔE. Since the total energy is a negative value, this means that in almost *all* cases, calculations made with basis sets containing diffuse functions give a better estimate[67] of the energy compared to calculations made with basis sets omitting them. This supports previous claims[21a,22b,d,26a] that diffuse functions are necessary for improving various energies calculated for anions.

Most molecules show an equal amount of negative and positive differences for $\Delta\delta_C$. However, PAHs show a slight bias towards positive differences, *i.e.* the ^{13}C-NMR shifts obtained using diffuse functions are larger than those obtained without them. For ^{1}H-NMR shifts, however, the picture is considerably different: the shifts are *almost always* larger for calculations made using basis sets *including* diffuse functions compared with those obtained using basis sets excluding them. In other words, $\Delta\delta_H$ is almost always positive. The picture *vis-à-vis* $\Delta\rho$ resembles that of ΔE. The use of basis sets containing diffuse functions almost always ($>95\%$ of values calculated) results in more negative values than using the same method and basis sets excluding them.

Conclusions

Rightfully so, diffuse functions have widely been recognized for some time as a tool necessary for efficiently calculating various properties of anions. High charge density affects numerous properties, such as bond length, energy, and electron affinity. However, PAHs may use their size and, apparently more importantly, their π-system, for dispersion of charge over the carbon skeleton, reducing Coulomb repulsion and stabilizing themselves.

Differences between using and not using diffuse functions while calculating parameters of geometry are considerably affected by the size of the molecule, but more so by the conjugational availability. We conclude that the use of diffuse functions for calculating geometrical parameters for PAH anions in general is unnecessary and does not improve the calculated results significantly.

Energy calculations are affected in much the same way. PAH anions show little difference whether their energies were calculated including or excluding diffuse functions. Diffuse functions almost always improve the calculated energy for PAH anions, although trivially.[67] It is therefore of reduced

importance using these functions when calculating total energy or geometrical parameters for PAH anions.

The effect on NMR shifts is quite different. For the most part, the absolute differences, $\Delta\delta$, are not insignificant, clearly demonstrating that diffuse functions are crucial in calculating NMR shifts, regardless of the nature of anion or nucleus in question. If actual absolute values are desired (for instance, if no experimental data is available), then accuracy is available only to a certain degree. If, however, the calculation is only meant to assist assignment, then, in most cases, *regardless* of whether ^{13}C- or ^{1}H-NMR shifts are being calculated, full assignment may be realized quite reliably through correlation between experimental and calculated values, without use of diffuse functions.

On the whole, charge density calculations show that $\Delta\rho$ is always smaller for PAH anions than for smaller, aliphatic ones. NBO calculations *do* appear to confirm the much lower charge density for PAH anions. However, lack of results due to technical difficulties[64] and for reasons stated in the computational details section[51] prevent us from making unequivocal conclusions in this regard, and caution should be taken in attempting to extrapolate from the results presented.

Some PAH anions exhibit irregularity regarding differences calculated; however, closer examination of these anomalies may provide insight as to why they are such, and chemical reasoning may elucidate aberrations. Irregularity of various points on such figures may thus possibly be a tool for ascertaining specific and distinct chemical properties of particular anions. Such comparisons may therefore assist in the realization of which properties are similar for PAHs and which are dissimilar.

Supporting information available

Isotropy values obtained for optimized TMS using the various methods (1 table), tables of data and statistics for indenyl anion exemplifying methodology (2 tables), tables of full data for all anions calculated with all comparisons made (21 tables), schemes for all parameters set for anions excluding indenyl anion (20 schemes), and all three analogous figures not presented in paper for all properties (18 total) are available.

Acknowledgements

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40 For comparison to experimental values, see later in text.

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