The ^{3}He NMR spectra of a [60]fullerene cation and some arylated [60]fullerenes

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The ^{3}He NMR spectra have been measured for the following compounds containing ^{3}He within the fullerene cage: symmetrical $C_{60}Ph_2$, unsymmetrical $C_{60}Ph_4$, $C_{60}Cl_6$, $C_{60}Ph_5Cl$, $C_{60}(4\text{-}FC_6H_4)_5Cl$, and the carbocation derived from the latter by the addition of $AlCl_3$. In general there is an increase in ^{3}He shielding with increased number of addends, and a decrease in shielding, relative to the precursor, on forming the cation.

Introduction

The use of ^{3}He NMR spectroscopy for aiding the characterisation of fullerene derivatives is proving to be a very valuable tool; the derivatives are prepared from the parent fullerene containing ^{3}He incarcerated within the cage.[1] Since the ^{3}He nucleus acts as a probe for ring currents in the fullerene framework, its shielding can be used as a criterion for aromaticity. In general, the more upfield the ^{3}He resonance the more aromatic the fullerene, and thus for example, the values for [60]- and [70]-fullerenes appear at −6.4 and −28.8 ppm respectively (upfield of dissolved ^{3}He),[2] showing [70]fullerene to be the more aromatic of the two. A recent notable development is the measurement of the spectrum for $i\text{-}^3HeC_{60}^{6-}$, the peak for which appeared at −48.7 ppm,[3] indicating, as had been predicted earlier,[4] that this anion is much more aromatic than the parent fullerene. This fact can be understood in terms of the substantially increased electron delocalisation, as apparent from the enhanced diatropic ring currents extending all over the anion.[4]

Recently we have described the first formation of the [60]-fullerene carbocations, $C_{60}Ar_5^+$ (Ar = Ph, $4\text{-}FC_6H_4$)[5] and given the anion data described above, it was of interest to ascertain the effect of cation formation upon the helium chemical shift, and to compare the observed shift with theoretical calculations. For a reference compound and carbocation precursor we chose $C_{60}(4\text{-}FC_6H_4)_5Cl$. We also measured the shifts for $C_{60}Cl_6$, $C_{60}Ph_5Cl$, $C_{60}Ph_2$ and $C_{60}Ph_4$ in order to determine the effects of chloro and aryl addends.

Experimental

i-^{3}He[60]fullerene was prepared as described previously,[6] and was converted to $i\text{-}^3HeC_{60}Cl_6$, symmetrical $i\text{-}^3HeC_{60}Ph_2$, unsymmetrical $i\text{-}^3HeC_{60}Ph_4$, $i\text{-}^3HeC_{60}Ph_5Cl$ and $i\text{-}^3HeC_{60}(4\text{-}FC_6H_4)_5Cl$ in the manner reported for the empty-cage compounds.[7] The samples were dissolved in either a 1 : 1 mixture of CS_2–CD_2Cl_2 or a 3 : 1 mixture of 1-methylnaphthalene–CD_2Cl_2, and the spectra obtained in the usual manner;[2] differences in solvent produced only trivial changes in the shifts (see Table 1). Aluminium chloride (4 mg) was added to the $i\text{-}^3HeC_{60}(4\text{-}FC_6H_4)_5Cl$ solution to form the cation,[5] just prior to measuring the spectrum.

It was planned to determine the extent to which the cation was free or existed as an ion pair, by use of the less potent Lewis-acid catalysts $SnCl_4$ and $FeCl_3$, and the more potent SbF_5. No evidence for either cation or ion pair formation was obtained by using $SnCl_4$, but $FeCl_3$ may give a cation (a red solution was formed on mixing the reagents). However, no spectrum could be obtained (not even for the reference ^{3}He) due to the magnetic effect of iron. A variation was tried in which the CD_2Cl_2 and reference ^{3}He were contained in an inner NMR tube, the sample and catalyst in an outer tube, but again no signal could be seen, not even for the reference which was thereby segregated from the catalyst. Use of SbF_5 produced an intractable mixture which was not amenable to spectroscopic examination.

Geometries of the model compounds $C_{60}H_2$, $C_{60}H_6$ and $C_{60}H_5^+$ were fully optimised in C_s symmetry at a gradient-correct level of density-functional theory, employing the exchange and correlation functionals according to Becke[8] and Perdew,[9] respectively, a standard 3-21 basis set,[10] and a medium sized grid (grid 3).[11] *Incar* (endohedral) chemical shifts were evaluated (as negative of the absolute shieldings) at the centre of mass of the carbon framework, employing a direct implementation[12] of the gauge-including atomic orbitals (GIAO-SCF) method, together with a polarised double-ζ basis on C and H, denoted DZP.[13] It has been shown that *incar* shieldings computed in this way for fullerenes are virtually identical to the $\delta(^3He)$ chemical shifts of the corresponding *incar* He compounds computed at the same level.[14] In addition, chemical shifts have been evaluated at the centre of each pentagon and hexagon, denoted NICS (nucleus-independent chemical shift).[15] These have proved to be useful for the identification of locally aromatic areas in fullerenes.[16] All computations were performed with the TURBOMOLE[17] program package, using IBM RS6000 workstations of the Organisch-chemisches Institut.

Results and discussion

The observed chemical shifts are collated in Table 1 together with values calculated using the hydrogenated species as models. The main features of these data are:

(i) In every case, addends cause an upfield shift of the spectrum, indicating that the derivatised [60]fullerenes are more aromatic than the parent compound itself. This is understandable because in each derivative there are a number of pentagonal rings each containing an sp^3-hybridised carbon. This reduces strain so that delocalisation of electrons in adjacent hexagons (and which places a double bond in the pentagon)

Table 1 Observed and calculated ^3He shifts for [60]fullerene derivatives

Compound	Chemical shift (δ_{He}) $C_{60}X_n$ observed	Calculated shift[a] $C_{60}H_n$ calculated
C_{60}	-6.4	
$C_{60}Cl_6$	-12.3^b	
$C_{60}Ph_5Cl$	-15.14	-17.7
$C_{60}(4\text{-}FC_6H_4)_5Cl$	$-15.04^{c,d}$	-17.7
$C_{60}(4\text{-}FC_6H_4)_5^+$	-12.61^c	-15.6
$1,4\text{-}C_{60}Ph_2$	-10.5	-14.1
Unsymmetrical $C_{60}Ph_4$	-14.4^e	

[a] *Incar* (endohedral) shift computed at the GIAO-SCF level. [b] Minor peaks were present at -12.15, -12.10 and -12.08 ppm due to unidentified by-products. [c] In 1 : 1 CS_2–CD_2Cl_2; all other measurements employed 3 : 1 1-methylnaphthalene–CD_2Cl_2. [d] The value is -15.16 in 3 : 1 1-methylnaphthalene–CD_2Cl_2, showing the solvent effect to be trivial. [e] A minor peak due to an unidentified isomer was present at -14.34 ppm.

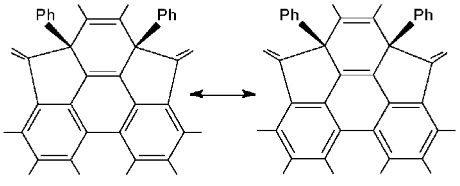

Fig. 1 Enhanced aromaticity in hexagons due to introduction of sp^3-hybridised carbons into adjacent pentagonal rings.

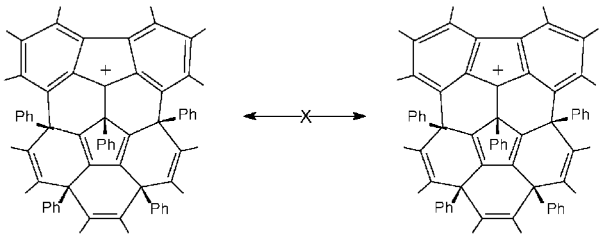

Fig. 2 Unfavourable delocalisation in the adjacent hexagons due to increase in sp^2 character of a pentagonal ring in $C_{60}Ar_5^+$.

becomes more favourable. This is illustrated for $1,4\text{-}C_{60}Ph_2$ in Fig. 1. Delocalisation will be increased the greater the number of addends, resulting in a larger upfield shift of the signal (greater aromaticity). This is most clearly illustrated by comparison of the shifts for $C_{60}Ph_2$ and $C_{60}Ph_4$.

(ii) Comparison of the results for $C_{60}Cl_6$ and $C_{60}Ph_5Cl$ shows that aryl and chloro addends produce a marked difference in aromaticity. This may be due to the electronegativity of the chloro addends reducing the *p*-character of the adjacent carbon and thus the overall aromaticity, by reasoning of (i). The small difference in effect between the pentaphenyl and penta(4-fluorophenyl) derivatives is consistent with this explanation, because the $-I$ (s-acceptor) effect of *para* F is very small (due to the long range) as shown by its modest σ_p-value of 0.06.[18]

(iii) The cation is less aromatic than the precursor molecule. This may be interpreted simply as the result of *increasing* the sp^2 character of one of the carbons in one of the pentagonal rings. This will reduce delocalisation in the adjacent hexagonal rings since a tendency towards anti-aromaticity in the pentagonal ring would thereby be created (Fig. 2). The resultant reduced delocalisation will lower the overall aromaticity of the cage.

(iv) Model calculations for the corresponding hydrogenated analogues correctly reproduce the *ca.* 2 ppm difference between the shift for the cation and its precursor. According to the computed NICS values in Fig. 3, and in accordance with the above-mentioned interpretation, the deshielding in going to the cation can be traced back to an increased paratropic ring current in the pentagon containing the cationic centre, and in particular to

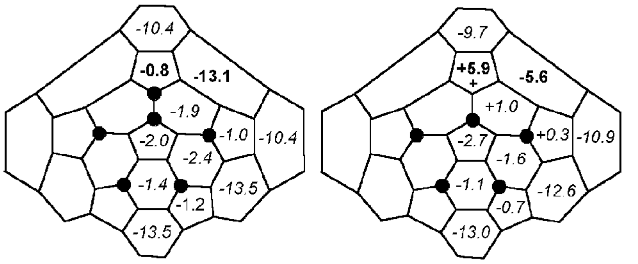

Fig. 3 NICS patterns in $C_{60}H_6$ (left) and $C_{60}H_5^+$ (right); negative and positive values denote local aromaticity and anti-aromaticity, respectively; values in boldface are those that undergo the largest changes.

the significant decrease of diatropic currents in two adjacent hexagons. The reduced aromaticity in the latter is consistent with that on going from benzene (NICS = -10.8) to the benzyl cation (NICS = -3.9). Note that the conjugated six-membered rings in the vicinity of the addends are indicated to be more aromatic than the hexagons in C_{60} [NICS = -6.6, NICS (pentagons) = 7.0]. The calculations also reproduce the lower shift for the $1,4\text{-}C_{60}H_2$ compared to compounds having six addends.

(v) Because the structure of unsymmetrical $C_{60}Ph_4$ is not known with absolute certainty, we have not calculated a shift value. For the 'standard' eight isomers obtained by double 1,2-addition of hydrogen across all possible [6,6]-positions,[19] values ranging from -12.6 to -14.9 are computed,[20] though of course these sites are not involved in unsymmetrical $C_{60}Ph_4$. Nevertheless, within the limits of the calculations, we could expect a value within this range, which agrees quite well with the observed result.

To conclude, we have measured the ^3He NMR spectrum for a [60]fullerene cation which is downfield shifted relative to that of the neutral precursor of the order predicted by calculation, and in contrast to the upfield shift reported previously for a [60]-fullerene anion. The ^3He NMR spectra for polyaddended [60]fullerenes show an upfield shift, again as calculated, and consistent with derivatised [60]fullerenes being more aromatic due to the greater delocalisation arising from the decrease in strain.

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