Methoxy and Methoxide Adducts of Fullerene-60: Semiempirical Theoretical Studies*

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Abstract

Semiempirical molecular orbital calculations utilising the AM1 approximation with the MOPAC program have been used to suggest the likely stable isomeric structures of the smaller methoxylated adducts of C_{60} , namely the anions $C_{60}(OMe)_n^-$, n = 1, 3, 5, 7, and the neutral species $C_{60}(OMe)_n$, n = 2, 4, 6. While the OMe species is expected to behave similarly to the F atom in respect of its electronegativity and electrophilicity, its greater size and asymmetric geometry influences the role of non-bonded interactions in determining the favoured configurations and relative chemical stabilities of the respective isomers of each structure. The 'string' model which describes the localised addition pattern observed in the case of the bromine adducts, $C_{60}Br_{2n}$, for n values up to 12, is also appropriate in describing the stable OMe and OMe⁻ adducts of C_{60} . The five-fold symmetric $C_{60}(OMe)_5^-$ anion is of particular interest as it is revealed as the most stable species, in agreement with its observation as the most abundant species occurring in electrospray mass spectra. This suggests that metal salts of the general type $M^+C_{60}L_5^-$ may be isolable under appropriate experimental conditions.

1. Introduction

Among the smaller molecular species which produce stable adducts of the buckminsterfullerene molecule, C_{60} , the methoxy radical, OCH_3 (or OMe), and its anion methoxide, OCH_3^- (or OMe^-), reveal a number of identified adduct molecules and ions. While the existence of a number of the uncharged polymethoxylated $C_{60}(OMe)_n$ compounds has only been inferred by mass spectrometric analysis showing n values varying from 1 to 26 (Olah *et al.* 1991), the series of anions $C_{60}(OMe)_n^-$ with n = 1, 3, 5, 7 has been observed by negative ion electrospray ionisation mass spectrometry (Wilson and Wu 1993). These latter, with their odd n values, are presumably stabilised through being of closed-shell electronic structure, which would also suggest that even n values should be favoured among the neutral species.

While none of these species has been isolated and characterised as a pure compound, spectroscopic studies, particularly of the ion species, can be contemplated. However, analogous to the halogen adducts of C_{60} , the OMe and OMe⁻ adducts are most amenable to theoretical study. While only a few halogen

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adducts of C_{60} have been structurally characterised, namely $C_{60}Br_6$, $C_{60}Br_8$ and $C_{60}Br_{24}$ by X-ray crystallography and Raman spectroscopy (Birkett *et al.* 1992, 1993; Tebbe *et al.* 1992), and $C_{60}F_{48}$ by NMR (Gakh *et al.* 1994), wide-ranging calculations of the F, Cl, Br and I adducts of C_{60} have been reported (Dixon *et al.* 1992; Matsuzawa *et al.* 1992*a*, 1992*b*; Peel and Rothwell 1994). These studies reveal the 'poly-alkene' nature of C_{60} in its chemical reactions, where addition of X₂ occurs at 1,2- and 1,4- sites analogous to halogen addition to ethylene and butadiene respectively. The loss or displacement of double-bond character, located initially in the hexagon-hexagon bonds of C_{60} , follows the expectation of simple valency rules, with the adduct-site carbon atoms undergoing considerable pyramidalisation.

While the OMe species can be regarded as possessing high electrophilicity and hence should exhibit a similar propensity for addition to C_{60} as the F atomic species, the polyatomic nature and hence physical bulk of OMe is expected to enhance the effects of non-bonded interactions in influencing the geometric structures available to isomers of the various poly-OMe adduct species under consideration.

2. Calculations

The semiempirical molecular orbital calculations reported here have been confined to the closed-shell (singlet spin) species, namely the neutrals $C_{60}(OMe)_n$ of even n, and the anions $C_{60}(OMe)_n^-$ of odd n. The calculations carried out with the MOPAC (Version $6 \cdot 00$) program (Coolidge and Stewart 1990) involved the use of the AM1 approximation, as used earlier in a study of the stable isomers of $C_{60}Br_{2n}$ (Peel and Rothwell 1994). The calculated heats of formation, total adduct binding energies and average OMe/OMe⁻ stabilisation energies of the geometry-optimised isomers considered are summarised in Table 1.

3. Results and Discussion

(3a) $C_{60}OMe^{-}$ and $C_{60}(OMe)_{2}$

The addition of a single OMe^- anion to C_{60} has various structural aspects of interest. The Me group will be expected to adopt conformation minimising non-bonded interactions with the nearest C_{60} atoms, and the distribution of the negative charge can be expected to relate to the variations in double-bond character experienced by the bonds in the vicinity of the adduct-site carbon atom. The diagrams in Fig. 1 illustrate the results obtained. The OMe unit adopts a minimum energy local geometry similar to that in dimethylether, Me₂O, with staggered electron lone-pairs and bond-pairs, but with the Me group located above a C_{60} hexagon in preference to a pentagon. A barrier to full rotation about the C–OMe bond is determined as 11 kJ mol⁻¹, though the chiral pair of structures with the Me group over adjacent hexagons can exchange through a smaller barrier of only 2 kJ mol⁻¹.

If the addition were to be considered as confined to the 1,2- double bond the second carbon would also be expected to pyramidalise and obtain the available negative charge. The charge distribution shown in Fig. 1 indicates that this is the major effect of the charge distribution, though the hexagon carbons located para to the OMe adduct also share some of the negative charge. This result

Molecule		ΔH_{f}	$\Delta H_{\rm b}*$	$\Delta H_{\rm a}^{*}$
C ₆₀		4073		
OMe ⁻		-161		
OMe		-14		
$C_{60}OMe^-$		3534	377	377
$\mathrm{C}_{60}(\mathrm{OMe})_2$	1,2-	3657	388	194
	1,4-A	3672	373	187
	1,4-B	3674	372	186
$C_{60}(OMe)_3^-$	A	3096	788	263
	В	3099	786	262
	\mathbf{C}	3126	758	253
	D	3125	760	253
	Е	3166	718	239
$C_{60}(OMe)_4$	Α	3242	776	194
	В	3242	776	194
$C_{60}(OMe)_{5}^{-}$		2615	1243	249
$C_{60}(OMe)_6$	А	2783	1209	201
	В	2783	1208	201
	С	2824	1167	195
$\mathrm{C_{60}(OMe)_7^-}$		2206	1624	232

Table 1. MOPAC/AM1 results for selected isomers of $C_{60}(OMe)_n^-$, n = 1, 3, 5, 7, and $C_{60}(OMe)_n$, n = 2, 4, 6

Heats of formation $\Delta H_{\rm f}$, heats of adduct binding $\Delta H_{\rm b}$, and stabilisation energies per OMe $\Delta H_{\rm a}$ are in kJ mol⁻¹

* $\Delta H_{\rm b}$ is for the reaction $C_{60}({\rm OMe})_m({\rm OMe}^-)_n \rightarrow C_{60}+m{\rm OMe}+n{\rm OMe}^-$; $\Delta H_{\rm a}$ is given by $\Delta H_{\rm b}/(m+n)$.

indicates that the structure can be interpreted as showing some 1,4- adduct character as well. However, analysis of the CC bondlengths in the vicinity of the OMe adduct shows that, while there are small movements of double-bond character into the appropriate hexagon 'single-bonds', the major effects are at the adduct-site carbon where its attached 'double-bond' expands from 1.385 to 1.491 Å, and the near-equivalent 'single-bonds' expand from 1.465 to 1.547 Å indicating considerable pyramidalisation.

The addition of two OMe units to C_{60} is expected to involve competition between the 1,2- and 1,4- isomer structures, with further variability in respect of the location of the Me group above appropriate hexagons with minimal steric interaction between the two OMe units being important. The calculated structures and relative energies are compared in Fig. 2. The lowest energy isomer is the 1,2- structure where the Me groups are constrained to locate above adjacent hexagons. However, steric repulsion results in each group rotating by 30° away from the central location exhibited in C_{60} OMe⁻. It is noted that this is also a chiral structure for which a barrier of 28 kJ mol⁻¹ exists for concerted symmetric rotation of both OMe groups to convert to its enantiomer. While there are numerous examples of chiral structures, both known and anticipated, among the higher fullerenes, the occurrence of chiral structures among simple adducts of C_{60} is only represented to date at the experimental level by the recent isolation of $C_{60}F_{48}$ (Gakh *et al.* 1994).

The two possible 1,4- isomers of $C_{60}(OMe)_2$ shown as structures A and B in Fig. 2 differ by only 2 kJ mol⁻¹ in energy, with the A isomer, that of slightly larger



Fig. 1. The C₆₀OMe⁻ anion showing aspects of its theoretical structure including local geometry of the OMe unit, potential energy curve (ΔH values in kJ mol⁻¹) for rotation of the Me group about the C₆₀-O bond, adduct binding energy ΔH_b in kJ mol⁻¹, a ball-and-stick model and the charge distribution (atom charges in milliprotons) in the vicinity of the adduct-site.



Fig. 2. The $C_{60}(OMe)_2$ molecule: theoretical structure of the lower energy isomers of 1,2and 1,4- types, with adduct binding energies ΔH_b in kJ mol⁻¹, and a ball-and-stick model of the favoured 1,2- isomer.

dipole moment (2.9 Debye compared with 2.6 D), exhibiting the greater stability. This 1,4- structure, which can be described as indicating 'string' character in the form of head-to-tail alignment of the OMe units over adjacent hexagons, is less stable by 15 kJ mol^{-1} than the 1,2- isomer, similar to the difference of 18 kJ mol^{-1} shown by the analogous $C_{60}F_2$ isomers (Matsuzawa *et al.* 1992*b*).

An approximate analysis of the comparative bonding strengths of the OMe and OMe⁻ groups, based on their respective AM1 heats of formation, indicates near equality for the total adduct binding energies represented by

$$C_{60}OMe^- \rightarrow C_{60} + OMe^- \qquad \Delta H = 377 \text{ kJ mol}^{-1},$$

 $C_{60}(OMe)_2 \rightarrow C_{60} + 2OMe \qquad \Delta H = 388 \text{ kJ mol}^{-1}.$

While this is an imperfect comparison it shows that delocalisation of the negative charge in $C_{60}OMe^-$ results in some additional stabilisation over the typical C–O bond energy of 358 kJ mol⁻¹ (Harrison 1974), while the average $C_{60}OMe$ bond energy of 194 kJ mol⁻¹ in $C_{60}(OMe)_2$ indicates considerable destabilisation from steric effects. These ΔH values will be used in later comparisons involving the larger $C_{60}(OMe)_n$ neutrals and anions.



Fig. 3. The $C_{60}(OMe)_3^-$ anion: theoretical structure of the lower energy isomers, with adduct binding energies ΔH_b in kJ mol⁻¹.

(3b) $C_{60}(OMe)_n^-, n = 3, 5, 7$

It is expected that the geometry favoured for $C_{60}(OMe)_3^-$ will have localised OMe groups related via 1,2- and/or 1,4- structural elements. If the three OMe groups adopt adjacent rather than remote locations on the C_{60} sphere, increased resonance stabilisation together with greater delocalisation of the negative charge would be anticipated. This appears to be the influence which favours the lowest energy isomer A, as illustrated in Fig. 3, which can be described as having a doubled 1,4- structure with 'string' character, as described earlier, providing additional stabilisation through the doubling effect. The calculation indicates virtual equivalence of the OMe groups in terms of their bondlength parameters and local charges, while the negative charge is concentrated symmetrically but on only two of the adjacent carbons, those ortho to the first and third OMe units in the 'string'. A similar structure, isomer B, is the next lowest in energy. By contrast 1,2- structures including separate remote locations of $(OMe)_2$ and $OMe^$ moleties appear to offer less stable configurations because of a reduced stabilising interaction between the three OMe units. A selection of isomers representing structures of this latter type, each with a 1,2- $(OMe)_2$ conformation, clearly show similar stabilities which vary reasonably smoothly with the separation of the two moieties. The minimum energy within these structures actually occurs for their greatest possible separation on the C_{60} sphere, indicating that an overall repulsion exists between the two adduct moieties. This is reflected in the total adduct binding energy for isomer C which is represented by

$$C_{60}(OMe)_{3}^{-}[C] \rightarrow C_{60} + 2OMe + OMe^{-1} \qquad \Delta H = 758 \text{ kJ mol}^{-1}$$

This ΔH value is slightly less than the sum, $377+388 = 765 \text{ kJ mol}^{-1}$, of the separate 20Me and OMe⁻ binding strengths defined earlier. The weak repulsion term indicated by the 7 kJ mol⁻¹ difference increases for structures with smaller separations, a maximum difference of 22 kJ mol⁻¹ occurring at the closer approach of the two moieties (isomer E) with slightly greater stability indicated by a difference of 9 kJ mol⁻¹ being achieved at intermediate distances (isomer D).

The most stable 'doubled 1,4- string' isomer A by comparison has a total adduct binding energy illustrated by

$$C_{60}(OMe)_{3}^{-}[A] \rightarrow C_{60} + 2OMe + OMe^{-} \qquad \Delta H = 788 \text{ kJ mol}^{-1},$$

showing 30 kJ mol⁻¹ greater stability than the most favoured $1,2-(OMe)_2/OMe^-$ structure, C above. This gives the important result that $C_{60}(OMe)_3^-$ is then stable relative to OMe⁻ transfer to C_{60} , since

$$C_{60}(OMe)_3^- + C_{60} \rightarrow C_{60}(OMe)_2 + C_{60}OMe^- \qquad \Delta H = 23 \text{ kJ mol}^{-1}$$

For $C_{60}(OMe)_5^-$ it is not surprising then that the 'closed string' or 'ring' structure, illustrated in Fig. 4, is of relatively high stability, and that the incorporation of a further 2OMe forming $C_{60}(OMe)_7^-$ is not greatly favoured. The lowest energy isomer of $C_{60}(OMe)_7^-$, shown in Fig. 4, is described as the $C_{60}(OMe)_5^-$ ring combined with a distant $(OMe)_2$ unit. This comparison is indicated by the ΔH values of the following exchange reactions:

$$\begin{split} & C_{60}(\text{OMe})_5^- + C_{60} \to C_{60}(\text{OMe})_3^- + C_{60}(\text{OMe})_2 \qquad \Delta H = 67 \text{ kJ mol}^{-1} \,, \\ & C_{60}(\text{OMe})_7^- + C_{60} \to C_{60}(\text{OMe})_5^- + C_{60}(\text{OMe})_2 \qquad \Delta H = -8 \text{ kJ mol}^{-1} \end{split}$$

The experimental electrospray ionisation mass spectra obtained by Wilson and Wu (1993) are consistent with this theoretical finding, as all of their reported negative ion spectra identify $C_{60}(OMe)_5^-$ as the most abundant species with $C_{60}OMe^-$ and $C_{60}(OMe)_3^-$ present in comparable though lesser amounts, but with $C_{60}(OMe)_7^-$ present in only very small or vanishing amounts. This experimental observation is then strongly supportive of the 'closed string' or 'ring' geometry suggested by the MOPAC/AM1 calculation for the $C_{60}(OMe)_5^-$ ion. This structure is illustrated as a ball-and-stick model (two views) in Fig. 4.



Fig. 4. The $C_{60}(OMe)_5^-$ and $C_{60}(OMe)_7^-$ anions: theoretical structure of the lowest energy isomers, with adduct binding energies ΔH_b in kJ mol⁻¹, and a ball-and-stick model (two views) of the highly favoured 'ring' isomer of $C_{60}(OMe)_5^-$.

(3c) $C_{60}(OMe)_n$ n = 4, 6

In comparing the favoured structures for $C_{60}(OMe)_4$ and $C_{60}(OMe)_6$ with $C_{60}(OMe)_2$, the value of the average OMe bonding energy, expressed in kJ mol⁻¹ per OMe, offers a simple quantitative criterion. As described earlier the preferred 1,2- adduct of $C_{60}(OMe)_2$ shows a bond energy of 194 kJ mol⁻¹ per OMe, and in constructing the higher neutral isomers from 1,2- $(OMe)_2$ pairs, the most stable structure of $C_{60}(OMe)_4$, isomer A, is that with remote pairs, which also show an average bond energy of 194 kJ mol⁻¹ per OMe. However, the 'string' structure, isomer B, with head-to-tail 1,4- additions, as illustrated in Fig. 5, exhibits exactly the same stability, shown by the same average bond energy of 194 kJ mol⁻¹ per



Fig. 5. The $C_{60}(OMe)_4^-$ and $C_{60}(OMe)_6^-$ molecules: theoretical structure of the lower energy isomers, with adduct binding energies ΔH_b in kJ mol⁻¹.

OMe. Isomers of slightly higher energy result when 1,2- pairs are brought closer together on the C_{60} sphere.

The likely isomers of $C_{60}(OMe)_6$ can be based on these two $C_{60}(OMe)_4$ structures with a structure analogous to the known structure of $C_{60}Br_6$ (Birkett et al. 1992) providing the lowest energy. This can be described as the $C_{60}(OMe)_5^-$ 'ring' with one of the OMe units coupling with the sixth OMe unit in a 1,2combination, but of overall neutral charge. While this structure for $C_{60}(OMe)_6$, which actually occurs as two isomers of very similar energy, A and B, as shown in Fig. 5, appears to be sterically crowded and is forced to locate one OMe unit over a C_{60} pentagon, the average bond energy of 201 kJ mol⁻¹ per OMe indicates these to be the most stable of all the neutral (even n) molecules considered [Computer disk-space limitations presently prevent a consideration of here. $C_{60}(OMe)_8$ structures.] The nearest energy $C_{60}(OMe)_6$ isomer C is also based on a 1,4- 'string', in this case being a $C_{60}(OMe)_4$ combined with a distant $1,2-(OMe)_2$. With an average bond energy of 195 kJ mol^{-1} per OMe, this is only marginally stabilised over the $C_{60}(OMe)_4$ structures. An isomer constructed of three separated $1,2-(OMe)_2$ pairs only achieves an average bond energy of 192 kJ mol^{-1} per OMe.

4. Conclusion

Among the small OMe adducts of C_{60} , the semiempirical MOPAC/AM1 calculations show that for the neutral (even *n*) species a $C_{60}(OMe)_6$ structure

analogous to that of the known $C_{60}Br_6$ molecule is most favoured. For the anionic adducts (odd *n*) the $C_{60}(OMe)_5^-$ structure of five-fold symmetry and equivalent OMe units is greatly energetically favoured over adjacent anion adducts. This agrees with recent experimental observations by electrospray mass spectrometry and suggests that metal salts of C_{60} of the general formula $M^+C_{60}L_5^-$ may be isolable under appropriate conditions.

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