Fullerenes

Generation and Properties of an Alkylated C_{70} Cation**

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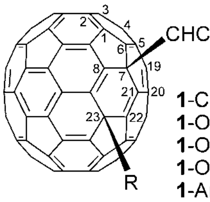
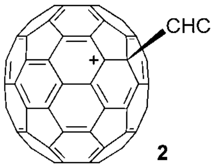
Despite the widely accepted notion that fullerenes are electronegative molecules, recent studies of functionalized C_{60} cations have led to the successful generation of monoalkylated $(RC_{60})^+$ ($R = CHCl_2$,[1] CCl_2CH_2Cl,[1] $CH_2P(O)(OEt)_2$[2]), protonated $(HC_{60})^+$,[3] and pentaarylated $(Ar_5C_{60})^+$ ($Ar = C_6H_5$, 4-FC_6H_4)[4] derivatives. The fact that C_{70} is slightly more susceptible to electrochemical oxidation than C_{60}[5] led us to expect that a monoalkylated C_{70} cation $(RC_{70})^+$ could also be generated as a long-lived cation and that its stability would be comparable to $(RC_{60})^+$. Unlike the anionic counterpart,[6] no derivatives of the C_{70} cation, $(RC_{70})^+$, have been prepared as directly observable species. One potential difficulty in the preparation of $(RC_{70})^+$ is the possible formation of a mixture of regioisomers owing to the presence of five different types of carbon atoms in the C_{70} cage. Here we report the generation and spectroscopic observation of the first alkylated C_{70} cation, obtained in an isomerically pure form, and a quantitative evaluation of its thermodynamic stability.

Treatment of C_{70} with $AlCl_3$ (70 equivalents) in carefully dried chloroform at 40 °C resulted in the addition of one molecule of chloroform, and the reaction reached completion within 1 hour. Separation of unconverted C_{70} (40 % recovered) by HPLC using a Buckyprep column gave the major product, **1**-Cl, in 27 % yield (45 % based on consumed C_{70}).



1-Cl: R = Cl
1-OH: R = OH
1-OMe: R = OMe
1-OTFE: R = OCH_2CF_3
1-An: R = 4-$MeOC_6H_4$



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The FAB mass spectrum of the adduct showed a peak for the molecular ion corresponding to the monoadduct. The ^{13}C NMR spectrum showed 68 carbon signals in the sp^2

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region ($\delta = 130$–154 ppm) and three signals in the sp^3 region ($\delta = 74.0$, 61.7, and 59.3 ppm), whereas the ^{1}H NMR spectrum showed a single peak at $\delta = 6.17$ ppm. These data indicate that the product is isomerically pure and that the molecule contains no symmetry elements. On the basis of these data, as well as the more rigorous discussion on the structure of the cation $(CHCl_2\text{-}C_{70})^+$ described below, the obtained adduct was assigned to the 23-chloro-7-dichloromethyl derivative **1**-Cl, in which the two addends are positioned across a six-membered ring located at the flat region of the C_{70} core.

Adduct **1**-Cl was converted into fullerenol **1**-OH in 63 % yield by passing it through a column of 230–400-mesh silica gel using CS_2 as the eluent. The hydrolysis, which presumably occurs owing to water contained in the silica gel, is regiospecific and gives only a single isomer that shows 68 aromatic ^{13}C signals, suggesting that **1**-OH is a structural analogue of **1**-Cl.[7] Fullerenol **1**-OH was readily soluble in CF_3SO_3H and gave a reddish brown solution of $(CHCl_2\text{-}C_{70})^+$. The ^{1}H NMR spectrum of the solution showed a singlet at $\delta = 5.59$ ppm. In the ^{13}C NMR spectrum (Figure 1), the cationic carbon center appears at $\delta = 198.16$ ppm, and two additional signals were observed at $\delta = 177.49$ and 175.81 ppm. The presence of 62 peaks for the other sp^2-hybridized carbon atoms indicates C_1 symmetry for the cation. In the sp^3 region, two signals ($\delta = 70.32$ and 64.82 ppm) were observed for the carbon atom in $CHCl_2$ as well as the carbon atom in the cage to which this group is directly attached.

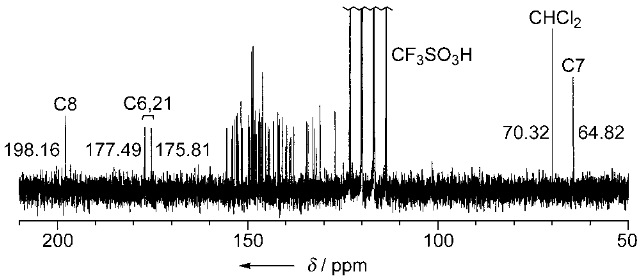

Figure 1. ^{13}C NMR spectrum of **2** (RT, 100 MHz, in CF_3SO_3H; [D_{12}]cyclohexane was used as an external standard). The assignment of the signal for the $CHCl_2$ group is based on DEPT measurements.

In the cation $(CHCl_2\text{-}C_{70})^+$, the $CHCl_2$ group is considered to be connected to one of the five types of carbon atoms (A–E) on the C_{70} cage, as illustrated in Figure 2a. The attachment of the $CHCl_2$ group at carbon centers C or D produces a nonsymmetrical (C_1) cation, while isomers which have an addend at carbon atoms A, B, or E are C_s-symmetric. Calculation of the relative energies of the five regioisomers by the DFT method (Table 1) showed that isomer D (Figure 2a) lies at the lowest energy and is 2.55 kcal mol^{-1} more stable than isomer C. The observed symmetry (C_1) and the calculated energies strongly support the conclusion that the generated cation is isomer D, that is, the 7-dichloromethylated C_{70} cation **2**.

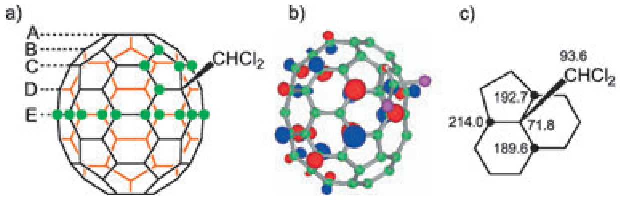

Figure 2. Results of DFT calculations for isomer D of $(CHCl_2\text{-}C_{70})^+$ (**2**): a) green dots represent carbon atoms that have a Mulliken charge greater than 0.025 (B3LYP/6-31G*); b) the LUMO (B3LYP/6-31G*); c) ^{13}C NMR chemical shifts (δ; B3LYP/6-311G**//B3LYP/6-31G*).

Table 1: Molecular symmetry and calculated relative energies of the regioisomers of $(CHCl_2\text{-}C_{70})^+$.

Isomer[a]	Symmetry[b]	Relative energy[c] [kcal mol^{-1}]
A	C_s	5.58
B	C_s	0.69
C	C_1	2.55
D (**2**)	C_1	0.00
E	C_s	15.96

[a] Position of the $CHCl_2$ group. [b] Time-averaged symmetry on the assumption of rapid rotation of the $CHCl_2$ group around the C_{70}–C bond. [c] Staggered conformations of the $CHCl_2$ group with respect to the C_{70}–C bond were assumed. Energies were calculated at the B3LYP/6-31G* level for all possible conformers, and that of the most stable conformer is presented for each regioisomer.

The observed preferential electrophilic attack to carbon atom D of C_{70} under Friedel–Crafts conditions ($CHCl_3/AlCl_3$) is consistent with the large HOMO coefficient of this carbon atom (Figure 3). This is in contrast to the fact that nucleophilic addition[6,8,9] and cycloaddition[8,10] to C_{70} favors carbon atoms A and B, which have the most pyramidal shape and large LUMO coefficients (Figure 3).

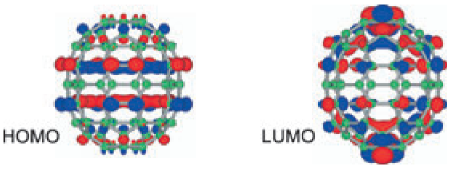

Figure 3. The HOMO and LUMO of C_{70} (B3LYP/3-21G).

A calculation of the NMR chemical shifts by the GIAO method (Figure 2c) showed that C8 ($\delta = 214.0$ ppm) is the most deshielded, whereas C6 ($\delta = 192.7$ ppm) and C21 ($\delta = 189.6$ ppm) are considerably more deshielded than the other sp^2-hybridized carbon atoms ($\delta = 134.4$–165.0 ppm), in qualitative agreement with the observed ^{13}C NMR spectrum. Mulliken charges are largely distributed on the carbon centers in region E and those surrounding the sp^3-hybridized carbon atom that bears the $CHCl_2$ group (Figure 2a, carbons marked by green dots), where the pyramidalization of the C–C bonds is relatively small. The total charge on these carbons is 0.88*e*.

Solutions of cation **2** in CF_3SO_3H showed a long-wavelength band with $\lambda_{max} = 991$ nm ($\varepsilon = 2020$ cm^{-1}M^{-1}; Figure 4), in analogy to $(CHCl_2\text{-}C_{60})^+$ (≈ 1200 nm).[1] Quenching of a solution of **2** in CF_3SO_3H by methanol yielded a single isomer of the methyl ether, $CHCl_2\text{-}C_{70}\text{-}OMe$, which has no molecular symmetry, as revealed by the observation of 72 signals in the

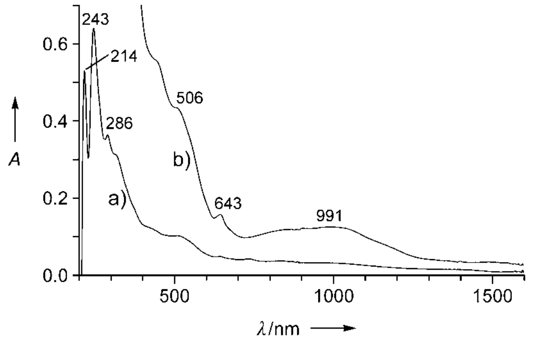

Figure 4. UV/Vis/NIR absorption spectra of **2** in CF_3SO_3H at room temperature (pathlength = 1 cm); a) 1.17×10^{-5} M; b) 5.90×10^{-5} M.

^{13}C NMR spectrum. Of the three carbon atoms in **2** over which the LUMO is mainly distributed, namely C8, C21, and C23 (Figure 2b), the methoxy group appears to attack at C23 because attack at other carbon atoms would produce sterically unfavored 1,2-isomers.[11,12] The resulting adduct, **1**-OMe,[7] is a derivative of 7,23-$C_{70}H_2$, which, on the basis of ab initio calculations, is the most stable derivative among the $C_{70}H_2$ isomers with nonadjacent hydrogen atoms.[13]

Cation **2** is stable in CF_3SO_3H at room temperature for over a week. The cation is also formed as a short-lived intermediate by the spontaneous ionization of the C_{70}–Cl bond under solvolytic conditions. Thus, in a solution of **1**-Cl in anisole/CF_3CH_2OH (9:1 v/v), the fullerene was slowly converted according to first-order kinetics into the S_N1 products **1**-An[7] (An = *p*-anisyl) and **1**-OTFE[7] (TFE = 2,2,2-trifluoroethyl) in a molar ratio of 1:5. The essentially identical free energies of activation for **1**-Cl and $CHCl_2$-C_{60}-Cl[14] (Table 2) indicate very similar stabilities for **2** and $(CHCl_2\text{-}C_{60})^+$.

In conclusion, the first functionalized C_{70} cation, $(CHCl_2\text{-}C_{70})^+$ (**2**), was generated as a long-lived species in isomerically pure form by ionization of the corresponding fullerenol in CF_3SO_3H. The structure of the cation was confirmed by NMR spectroscopic analysis and DFT calculations. The thermodynamic stability of **2** was comparable to those of $(CHCl_2\text{-}C_{60})^+$ and the *tert*-butyl cation,[15] as revealed by solvolysis rate measurements.

Experimental Section

Full details of experimental procedures and spectroscopic data for new compounds are given in the Supporting Information. **1-Cl**: $AlCl_3$ (1.03 g, 7.72 mmol) was added to a solution of C_{70} (97.4 mg, 0.116 mmol) in dry $CHCl_3$ (120 mL) at 40 °C. The mixture was stirred for 50 min and quenched with cold water (100 mL). The usual workup and separation by HPLC (Buckyprep, toluene) afforded **1**-Cl as a dark-brown solid (30.5 mg, 27 %). **1-OH**: Compound **1**-Cl (30.5 mg, 31.8 μmol) was passed through a column of silica gel (230–400 mesh, 20-mm inner diameter × 300 mm) using toluene/hexane (2:1; 20 mL min^{-1}) as eluent to give fullerenol **1**-OH as a dark solid (19.0 mg, 63 %). Generation of **2**: A solution of **1**-OH (13.5 mg, 14.3 μmol) in CF_3SO_3H (1 mL) was placed in a 5-mm outer diameter NMR sample tube, and the ^1H and ^{13}C NMR spectra of the resulting reddish brown solution of **2** were recorded at room temperature.

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Table 2: Rate constants and activation parameters for the solvolysis of **1**-Cl and $CHCl_2$-C_{60}-Cl[a] in anisole/2,2,2-trifluoroethanol (9:1 v/v).

Substrate[b]	Intermediate	T [°C]	k_1[c] [10^{-6} s^{-1}]	$\Delta H^{\ddagger}$ [kcal mol^{-1}]	$\Delta S^{\ddagger}$ [cal mol^{-1} K^{-1}]	$\Delta G^{\ddagger}_{25°C}$ [kcal mol^{-1}]
$CHCl_2$-C_{70}-Cl (**1**-Cl)	$(CHCl_2\text{-}C_{70})^+$ (**2**)	25.0	12.3	11.1	−44	24.1
		50.0	56.6			
$CHCl_2$-C_{60}-Cl	$(CHCl_2\text{-}C_{60})^+$	25.0	14.6	10.6	−45	24.0
		50.0	62.6			

[a] See reference [14]. [b] Initial substrate concentration: 1.5×10^{-4} M. 2,6-Lutidine (1.5 equiv) was added as a buffer to suppress the reverse reaction. [c] Experimental error: ±5 %.

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