

Crown Ether Fulleroids and their Detection in Solution by Electrospray MS

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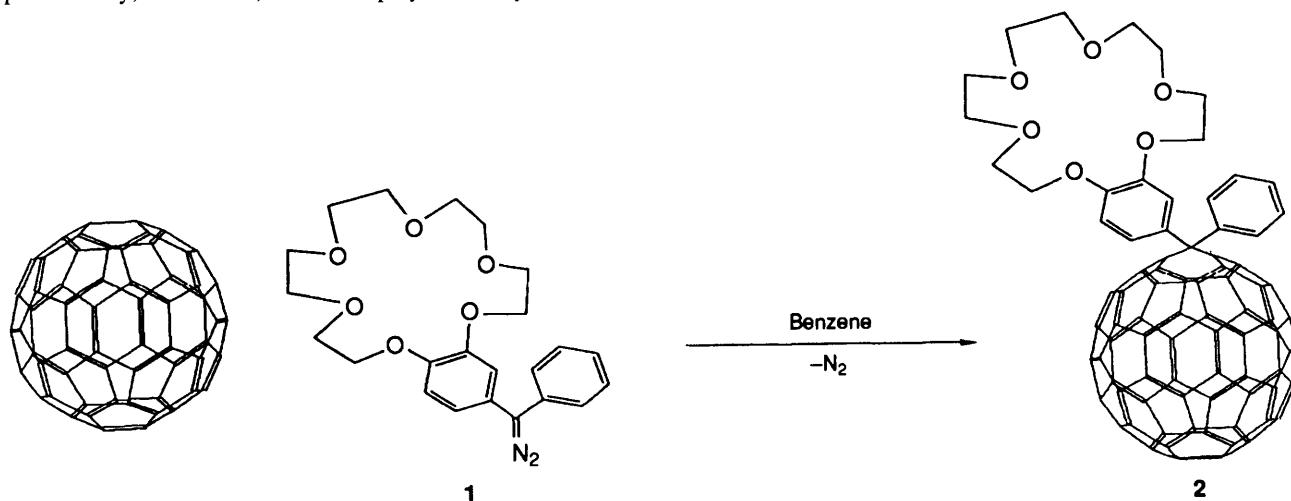
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The attachment of a crown ether to the surface of fullerene molecules facilitates their detection by electrospray mass spectrometry.

The explosion of fullerene chemistry continues unabated.¹ Recent reports on C₆₀ generation,² purification³ and chemical reactivity⁴ points out the need for better methods of identification. One problem facing the C₆₀ chemist is that solution characterization must be done primarily by ¹³C NMR. UV spectra of C₆₀ and its relatives are often identical.⁵ Mass spectrometry, of course, has also played a major role in

identification,⁶ but is difficult for many fullerene derivatives and generally is not feasible for detection of species in solution.

We have been studying applications of the new technique of electrospray ionization MS (ESI-MS) to organic chemistry⁷ and have reported a new reagent for ESI-MS detection of vitamin D.⁸ We have determined that crown ether tags



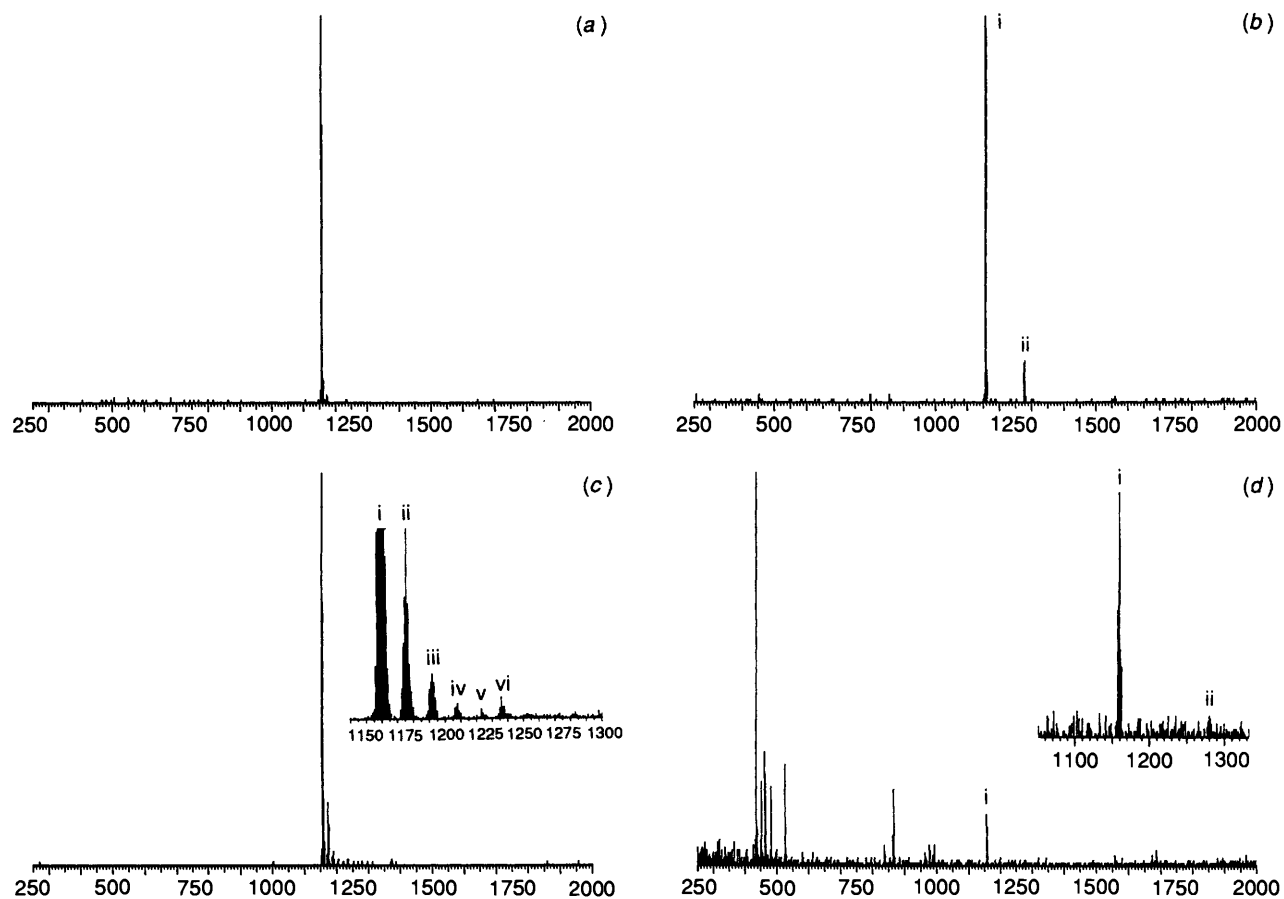


Fig. 1 Electrospray ionization MS spectrum in benzene-methanol containing KOAc: (a) reaction of compound **1** with purified C_{60} , MK^+ ; (b) reaction of compound **1** with commercial C_{60}/C_{70} mixture (9:1), i, MK^+ , ii, $M'K^+$; (c) overnight air oxidation of **2** in the presence of basic alumina, i, MK^+ , ii, MOK^+ , iii, MO_2K^+ , iv, MO_3K^+ , v, MO_4K^+ , vi, MO_5K^+ ; (d) reaction of compound **1** with crude soot, i, MK^+ , ii, $M'K^+$, where $M = C_{61}$ fulleroid **2**, $M' = C_{71}$ fulleroid. Peaks between m/z 400 and 1000 are byproducts of reagent **1**.

become charged as their Na^+ or K^+ adducts during ESI-MS and provide a convenient and highly sensitive method for ESI-MS analysis of neutral molecules.

Prompted by the recent report on cyclopropanation⁵ of C_{60} , we prepared diazo-crown reagent **1**[†] and allowed it to react with pure C_{60} in benzene to provide adduct **2**[‡] (42% yield). After addition of a methanol solution of KOAc ($\approx 10^{-3}$

[†] Compound **1** was prepared by formylation of benzo-18-crown-6, followed by phenyllithium addition and Jones oxidation. Hydrazone formation and oxidation with activated MnO_2 gave **1** as a purple oil which may be kept for several months in the freezer.

[‡] **Preparation of 2:** To a solution of 280 mg (0.388 mmol) of C_{60} ¹⁵ in 230 ml of benzene in ice-water bath (5–10 °C) 110 mg (0.257 mmol) of **1** in 50 ml of benzene was added dropwise within 1 h under nitrogen and the mixture was stirred for 2–3 h. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, toluene, then toluene-methanol = 8:1) to separate the adducts and unconverted C_{60} (190 mg recovered). Further separation of mono- and bis-adducts by prep-TLC (silica gel, toluene-methanol = 2:1) gave 120 mg of **2** as a dark-brown solid (42%, 85% based on recovered C_{60}). R_f (silica gel, toluene-methanol = 8:1) = 0.33. FAB-MS: m/z (% base) 720 (100, $[M-crown]^+$), 1120 (15, M^+), 1143 (45, $[M + Na]^+$) and 1159 (10, $[M + K]^+$). UV/VIS (λ_{max} , cyclohexane) 212, 261, 330, 424, 490, 528, 600, 696 nm. IR ν/cm^{-1} (KBr): 3023w, 2910m, 2854m, 1588w, 1511m, 1448m, 1420w, 1251m, 1124s, 1054m, 948w, 800w, 730w, 695m, 527s. ¹H NMR (300 MHz, CS_2 - $[^2H_6]$ acetone/3:1, δ): 8.10 (d, J 8.4 Hz, 2H), 7.63 (m, 1H), 7.46 (t, 2H), 7.28 (t, 1H), 6.92 (s, 1H), 6.67 (d, J 8.1 Hz, 1H), 4.05 (t, 2H), 3.98 (t, 2H), 3.74–3.80 (m, 4H), 3.52–3.56 (m, 12H). HRMS Calc. for $C_{83}H_{28}O_6$: 1120.189; Found: 1120.191.

mol dm^{-3}), injection of 5 μl min^{-1} of the 4:1 benzene: methanol solution of **2** into the ESI-MS[§] gave the spectrum in Fig. 1(a). This spectrum shows only the molecular ion $M + K^+$ in solution with no trace of fragmentation. This result is expected from ESI-MS which is the mildest possible ionization process (this also contrasts with FAB which shows loss of the crown ether side chain as the base peak). In a similar way, a commercial C_{60}/C_{70} mixture¹⁰ ($\approx 9:1$) provided the spectrum shown in Fig. 1(b). Our reagent **1** has also been used to detect C_{60} oxidation¹¹ [Fig. 1(c)] as well as to measure the C_{60}/C_{70} contents of soot by direct derivatization [Fig. 1(d)].

Besides a sensitive method for detection of C_{60} in solution, compound **2** is an important compound for two other reasons. Since it has been reported^{4b} that ' C_{61} -fulleroids' such as **2** have similar reactivity to C_{60} itself, one can use **2** to study fullerene reactions in solution. For example, we have used **2** to examine several 1,3-dipolar addition reactions, and can observe formation and nitrogen loss from up to five pyrazoline units from addition of alkyl azides to **2**.¹² The reaction of **2** with an excess of ethyl diazoacetate show results typical of such a study. After 1 h at 5–10 °C, only a trace of monoadduct was observed (inset, Fig. 2), but warming to room temp. leads to rapid addition of diazoacetate units. Fig. 2 showed the reaction mixture after 2 h indicating formation of up to tetra-adducts (Fig. 2, peaks ii–v) mainly without loss of nitrogen. Minor products from single N_2 loss (Fig. 2, peaks vi–viii) and multiple N_2 loss (Fig. 2, peaks ix–xi) may also be observed. In a similar way, we have followed other reactions

[§] The ESI-MS measurements were performed on a Vestec Model 200 single-quadrupole electrospray ionization mass spectrometer.

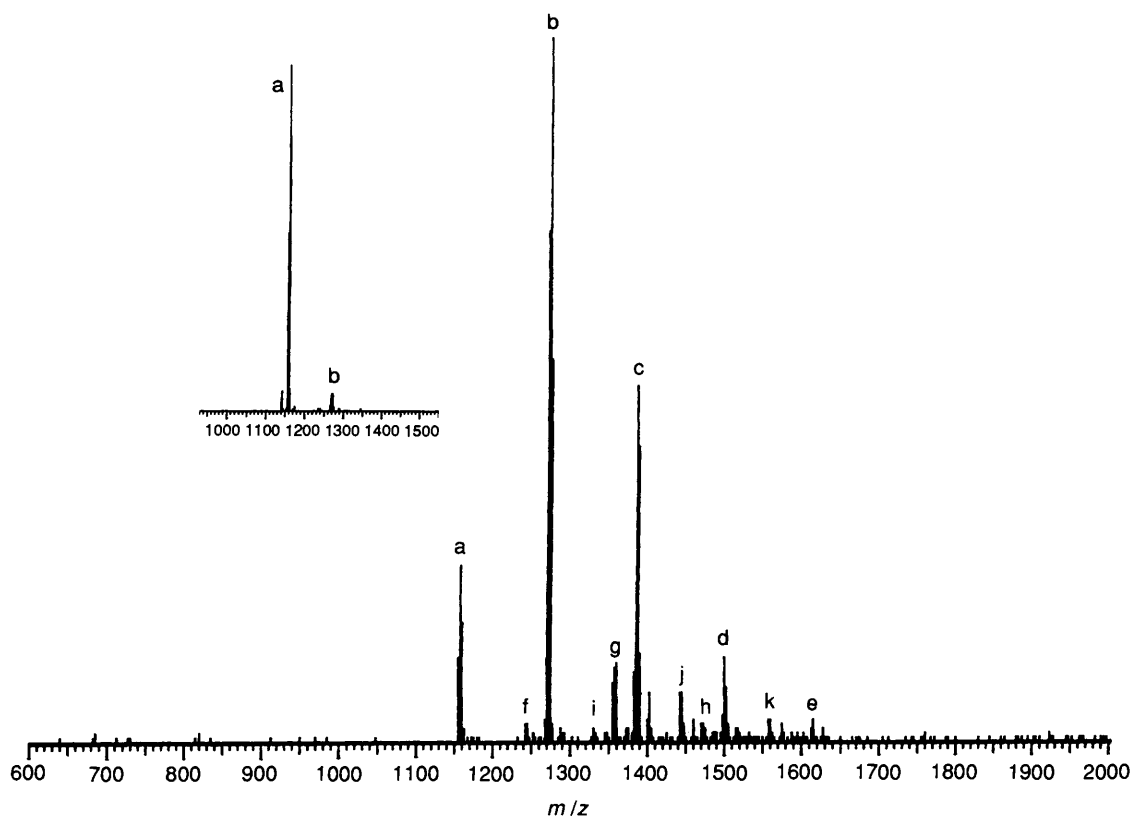


Fig. 2 Electrospray ionization MS spectrum of the reaction of **2** with an excess of ethyl diazoacetate (Aldrich) in benzene. Aliquots were withdrawn, diluted with benzene and 10^{-3} mol dm^{-3} KOAc in methanol and infused at $ca. 5 \mu\text{l min}^{-1}$ into the ESI-MS. Inset shows reaction progress after 1 h at $5-10^\circ\text{C}$, a, MK^+ , b, MXK^+ . After 2 h at 25°C , a, MK^+ , b, MXK^+ , c, MX_2K^+ , d, MX_3K^+ , e, MX_4K^+ , f, $\text{M}[\text{X}-\text{N}_2]\text{K}^+$, g, $\text{M}[\text{X}_2-\text{N}_2]\text{K}^+$, h, $[\text{MX}_3-\text{N}_2]\text{K}^+$, i, $\text{M}[\text{X}_2-2\text{N}_2]\text{K}^+$, j, $\text{M}[\text{X}_3-2\text{N}_2]\text{K}^+$, k, $\text{M}[\text{X}_4-2\text{N}_2]\text{K}^+$, where $\text{M} = \text{C}_{61}$ fulleroid **2** and $\text{X} =$ pyrazoline.

in solution including bromination, hydroboration, the Diels-Alder reaction and $[2 + 2]$ photocycloaddition.

Finally, the crown ether fulleroid **2** forms the expected host-guest complexes¹³ including the selective binding of alkali metals and ammonium salts. Metal salts and related complexes of fullerenes are of intrinsic interest as superconducting materials¹⁴ and compound **2** represents, as far as we are aware, the first fullerene containing a binding site for alkali metals.

In conclusion, we have shown that C_{60} and its relatives may be tagged using reagent **1** and detected in solution by ESI-MS. Studies of metal complexes of C_{61} -crowned fullerenoids and the general examination of fullerene reactions by ESI-MS will be reported in the near future.

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