The structure and reactivity of C\textsubscript{60}

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Abstract: C\textsubscript{60} contains thirty double bonds endocyclic to the twenty adjacent hexagons and exocyclic to the twelve isolated pentagons which comprise the highly symmetric, f\textsubscript{\text{1\textsubscript{\text{3\textsubscript{1}}}}} structure. As a result the cage exhibits chemical properties commensurate with those of an electron-deficient polyene.

Evidence for the existence of C\textsubscript{60} (Buckminsterfullerene) was first obtained in 1985 (1) and macroscopic quantities of this all-carbon molecule, together with small amounts of the higher fullerene C\textsubscript{70}, became available five years later by solvent extraction and chromatographic separation (2) of the sooty deposit resulting from the resistive heating and vapourisation of graphite (3). All carbons in C\textsubscript{60} are chemically equivalent, as revealed by \textsuperscript{13}C n.m.r. spectroscopy (2), however the structure contains thirty localised ‘double’ (ca.1.39 Å) and sixty ‘single’ (ca.1.44 Å) bonds; the double bonds are arranged exocyclic to the pentagons (4).

\text{C\textsubscript{60}} displays typical electron acceptor properties. For example, it exhibits six reversible one electron reductions in solution (5), commensurate with the filling of a triply degenerate low lying t\textsubscript{\text{1\textsubscript{\text{3\textsubscript{1}}}}} LUMO. Group 1 and 2 metal salts of C\textsubscript{60} are superconducting with transition temperatures (T\text{c}) 33 K for RbCs\textsubscript{2}C\textsubscript{60} (6) and 8.4 K for Ca\textsubscript{2}C\textsubscript{60} (7). Electroreduction of C\textsubscript{60} in the presence of [Ph\textsubscript{4}P\textsuperscript{+}][Cl\textsuperscript{-}] yields the mixed salt [Ph\textsubscript{4}P\textsuperscript{+}][C\textsubscript{60}][Cl\textsuperscript{2\textsubscript{-}}] (8), whilst the one-electron reductant, Cr\textsuperscript{III}(tpp) (1), gives [(I\textsuperscript{+})[C\textsubscript{60}][THF]]\textsubscript{3}. In the latter, THF stabilises the Cr\textsuperscript{III} oxidation state through solvation, whereas the Cr\textsuperscript{II} containing neutral salt is favoured in toluene (9).
The C$_{60}$ cage is susceptible to nucleophilic attack, but the degree of addition is difficult to control. For example, the mass spectrum of C$_{60}$Me$_n$, obtained by quenching C$_{60}$ with MeI, reveals the presence of species up to $n = 24$, with C$_{60}$Me$_6$ and C$_{60}$Me$_8$ dominant (9). By contrast, careful treatment of C$_{60}$ with one equivalent of eg. t-BuLi (10) followed by protonation yields two mono-adducts, C$_{60}$RH (R = t-Bu, (2) and (3)); (2) slowly rearranges to the thermodynamically favoured isomer (3) which contains no pentagonal double bond (11).

Liquid bromine reacts with C$_{60}$ to give C$_{60}$Br$_{24}$ in which all bromines are equivalent (12) (Schlegl diagram: 24 is the maximum number of bromines which can be attached to the cage so as to avoid occupation of adjacent sites). Bromination in CS$_2$ yields C$_{60}$Br$_6$, whereas in benzene or CCl$_4$ C$_{60}$Br$_6$ is formed (13). Treatment of C$_{60}$ with ICl gives C$_{60}$Cl$_6$ which is isostructural with the bromine analogue (14).

C$_{60}$ reacts with benzene in the presence of Br$_2$ and FeCl$_3$ to give mixed products including C$_{60}$Ph$_6$ (15), C$_{60}$Ph$_5$H (4) and C$_{60}$Ph$_{12}$ (16), based upon mass spectral evidence. Reaction of C$_{60}$Cl$_6$ with benzene and FeCl$_3$ gives C$_{60}$Ph$_5$Cl (5) which is readily reduced to (4) (17).
Benzyl radicals react with $C_{60}$ to give $C_{60}(\text{CH}_2\text{Ph})_n$ ($n \leq 15$) (18). E.s.r. spectra reveal the presence of allyl and cyclopentadienyl sites on the cage, a result which may have a bearing on possible intermediates in the bromination of $C_{60}$.

R = PhCH$_2$

Cycloadditions of dipoles and dienes (Diels Alder reaction) to $C_{60}$ have proved to be a particularly fruitful area of research and offer what is arguably the best way to date of developing the organofunctional chemistry of $C_{60}$. For example, one or more (up to six) diaryldiazomethane units add across the interpentagonal bonds to give pyrazolines which spontaneously lose $\text{N}_2$ to generate the diarylhomofullerene, $C_{60}\text{CAr}_2$ (6) (19). This strategy has been employed to prepare $C_{60}$ containing polymers (20) and, using a diazirine (carbene precursor) to attach a protected glycoside residue indirectly to the cage (7) (21).

Retro-Diels Alder processes can often be troublesome. For example, the cyclopentadiene adduct of $C_{60}$ decomposes upon heating unless the double bond in the addend is saturated (22). With diene (8), subsequent CO loss from the initial product of cycloaddition leads to formation of a stable aromatic ring (9) (23).

Transition metals have played an important role in the development of $C_{60}$ chemistry. Reaction with OsO$_4$ in the presence of 4-tert-butylpyridine (L) gave the osmyl ester $C_{60}[\text{OsO}_4\text{L}_2]$ (10), the first $C_{60}$ derivative to be fully characterised (24). The structures of five isomeric bis-osmyl esters have been deduced from their n.m.r. spectra (25). The platinum complex
C$_{60}$Pt(PPh$_3$)$_2$ (11) exhibits the properties commonly associated with eta-2 compounds (26); hexa-adducts, C$_{60}$[M(PEt$_3$)$_2$]$_6$ (M = Ni, Pd and Pt), with the metals disposed octahedrally around the cage, have been prepared (27).

REFERENCES