Formation and Stabilisation of the Hexa-cyclopentadiene Adduct of C60

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Up to 6 equiv. of cyclopentadiene react with C_{60}, and the resulting Diels–Alder adducts can be stabilised towards degradation during mass spectrometric analysis by hydrogenation of the pendant bicyclopentene moieties; stabilisation can also be affected by bromination.

Interpentagonal (6:6) bonds in C_{60} participate readily in cycloadditions,[1] but the potential of such reactions as a route to fullerene derivatives (and in particular their analysis by mass spectrometry) is restricted by the ease with which the adducts revert to starting materials. One solution to the problem employs dipolar reagents such as diazoalkanes[1] and azides,[2] whereby the heterocyclic products preferentially extrude dinitrogen, generating methano- and aza-fullerenes, respectively, or their fulleroid isomers. Yet another approach, relevant in the Diels–Alder context, has been to use o-quino-dimethane,[3] or a derivative,[4] whereby the aromatic character developed in the adduct acts as a disincentive to cyclorever-sion.

Although the prospect of obtaining mass spectra of cyclo-addition products through the use of the MALDI-TOF (matrix-assisted laser desorption ionisation–time of flight) procedure holds promise, this technique is still in its infancy and requires dedicated instruments, which are not widely available. Moreover, whilst it may be possible to obtain mass

spectra for adducts containing only one or two addends, matrix-solubility difficulties may emerge for fullerenes pos-sessing large numbers of addends. This problem led us to seek a solution applicable to existing instrumentation.

To date, the literature contains only one detailed report of a reaction between cyclopentadiene and C_{60}.[5] The structure of the mono-adduct product (confirmed by NMR) showed that addition occurs across one of the interpentagonal (6:6) bonds of a pyracyclene unit. The presence of six such units in C_{60}, distributed in an octahedral array,[6] and the observation of octahedral coordination of six $(Et_3P)_2M$ (M = Pt, Pd, Ni) entities to C_{60},[7] led us to anticipate that six cyclopentadiene molecules could be combined with C_{60}. Moreover, we were encouraged by the recent report that in a [2 + 2] cycloaddi-tion, six benzyne molecules, which are converted on addition to stable o-phenylene moieties, can be attached to C_{60}.[8]

We now report the successful reaction of six cyclopenta-diene units with C_{60}, and the stabilisation of the products against the retro-reaction during both FAB and EI mass
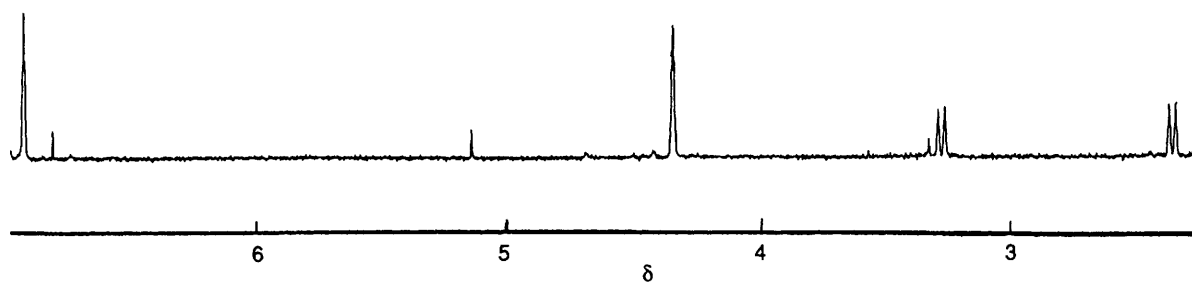
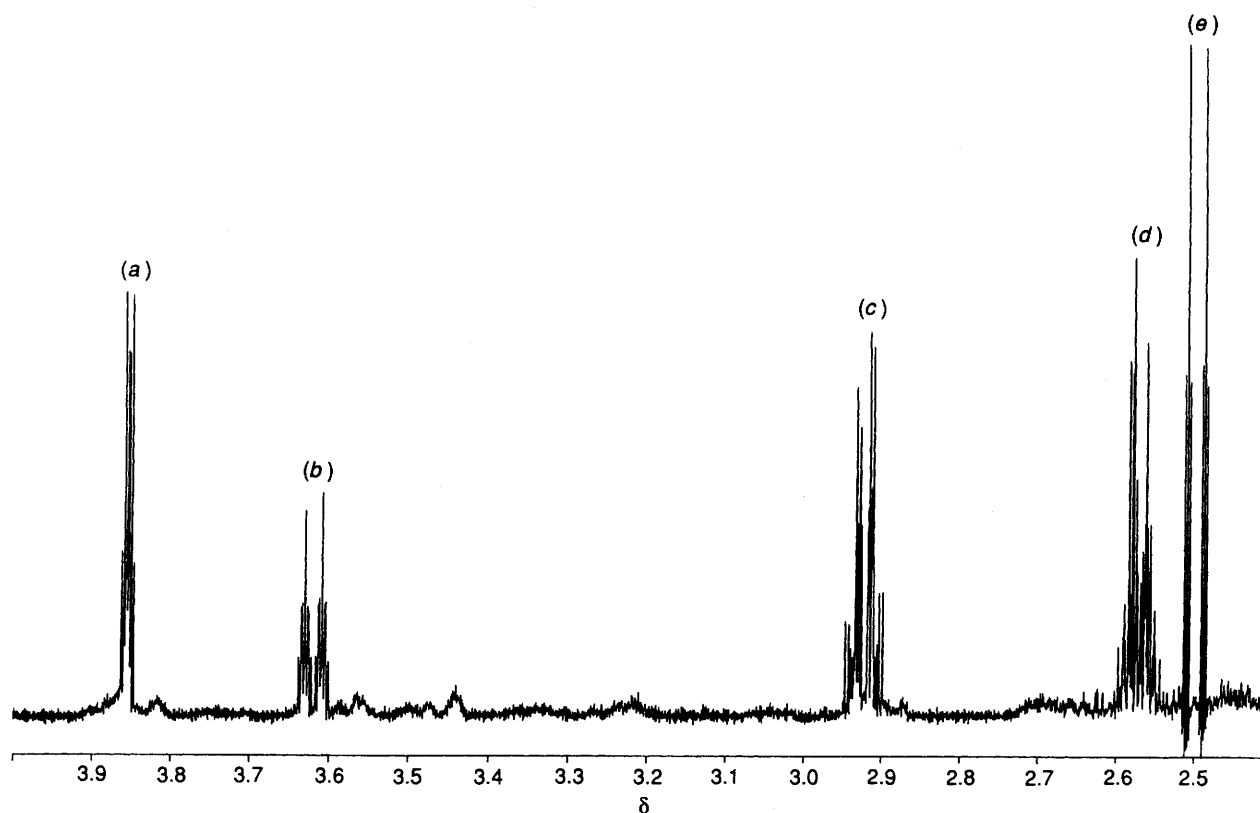Fig. 1 ^1H NMR spectrum ($CDCl_3$; 500 MHz) of the adduct of cyclopentadiene with C_{60}

Fig. 2 ^1H NMR spectrum ($CDCl_3$; 500 MHz) of the reduced adduct of cyclopentadiene with C_{60}

spectrometry, by selective hydrogenation of the pendant groups. We have confirmed the selectivity of this reduction by detailed ^1H NMR spectroscopy of the monoadduct, and we have also stabilised the monoadduct by selective bromination of the addend. We believe this development will be of significant value in the Diels–Alder chemistry of fullerenes. Our method relies on two features: first, whereas C_{60} is reduced by hydrogen in the presence of Pt/C, it is not reduced if Adam's catalyst is employed;[9] secondly, C_{60} does not react with bromine in dilute solution.[10]

Freshly distilled cyclopentadiene (1 equiv.) was added by microlitre syringe at room temp. to C_{60} dissolved in benzene, and the solution changed from the characteristic magenta to red–brown within 10 min. The mixture was stirred for 13 h, then filtered through a short column of alumina to remove any unconverted C_{60} (though none was observed). Removal of solvent under reduced pressure left pale-brown microcrystals the ^1H NMR spectrum (500 MHz), (Fig. 1) of which exhibited four resonances consistent with the C_5H_6 addend: δ ($CDCl_3$) 6.92 (2H, t, J 1.5 Hz, CH=), 4.35 (2H, t, J 1.5 Hz, CH), 3.27 (d, J 9.7 Hz, CH_2), 2.35 (d, J 9.7 Hz, CH_2); these values are all 0.15 ± 0.01 ppm upfield from those reported recently for this derivative (tetrachloroethane).[5]

A benzene solution of this material was stirred rapidly with Adam's catalyst under hydrogen (75 mmHg overpressure) for
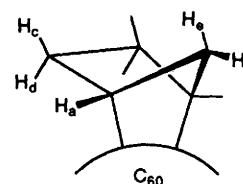

Fig. 3 Assignments of the resonances shown in Fig. 2

1 h, which resulted in the uptake of 1 equiv. of hydrogen. Filtration and removal of solvent by evaporation yielded brown material, which exhibited a prominent parent ion at m/z = 788 $[C_{60}(C_5H_8)^+]$ in the mass spectrum. The ^1H NMR spectrum (500 MHz) showed five resonances [Fig. 2(a)–(e)] at δ ($CDCl_3$) 3.85(5) (2H, dt, J 4.4 and 1.7 Hz), 3.620 (1H, dtt, J 10.8, 2.67 and 1.67 Hz), 2.92 (2H, m), 2.57 (2H, m) and 2.50 (1H, dt, J 10.8 and 1.65 Hz). The most downfield resonance was assigned to the bridgehead hydrogen atoms H_a (Fig. 3), the signal being upfield relative to that in the alkene precursor owing to the $sp^2 \rightarrow sp^3$ conversion of the adjacent carbon atoms. Spin-decoupling experiments showed H_a to have 1.7 Hz couplings to H_b and H_e, and 4.4 Hz coupling to H_c; no coupling was observed to H_d because the vicinial angle here is close to 90°. The multiplets at δ 3.620 and 2.923 were assigned
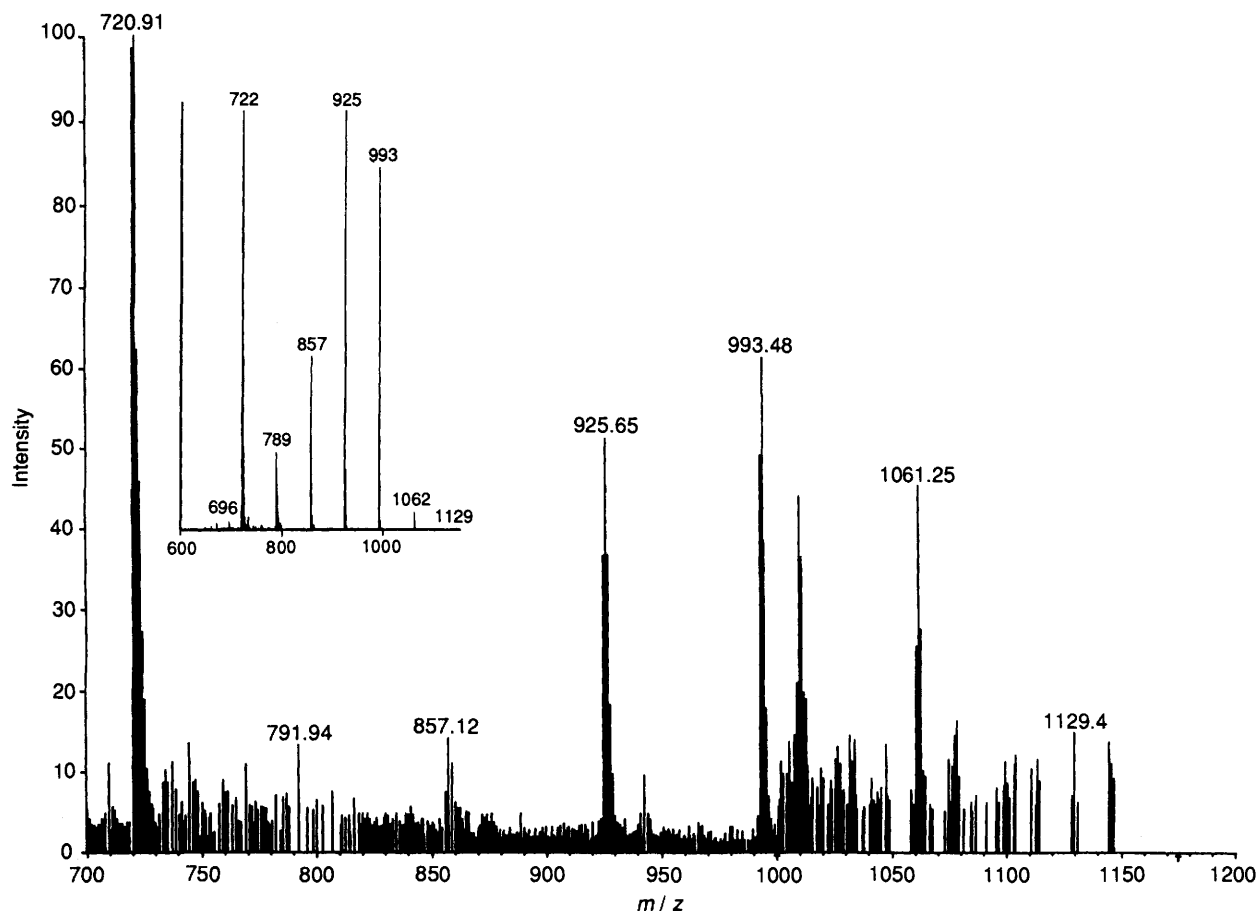
Fig. 4 FAB and (inset) EI mass spectra of the reduced hexa-cyclopentadiene adduct of C_{60}. The sensitivity in the FAB spectrum is multiplied fivefold between m/z 1000 and 1175. The poor sampling of data at m/z = 791.94 is due to swamping of the acquisition interface. The EI spectrum is normalised to the peak at m/z = 925.

to H_b and H_d, respectively, as spin-decoupling showed a 2.4 Hz W coupling between them. The H_c and H_d multiplets are complex owing to magnetic inequivalence and have not been fully analysed. H_b and H_e show a larger coupling constant (10.8 Hz) compared with the unreduced material (9.7 Hz).

Treatment of the initial Diels–Alder product with 1 equiv. of bromine in benzene gave a product, formulated as $C_{60}C_5H_6Br_2$, on the basis of the EI mass spectrum [main peaks were observed at m/z = 944, 946, 948 (1:2:1 intensity ratio)]. Unassigned peaks at m/z = 773, 789 and 857 were also present, together with $C_{60}O$.

If the cycloaddition was carried out as above, but using either 6 or 10 equiv. of cyclopentadiene, the mass spectrum of the reduced product revealed that four and six addends, respectively, had attached to the cage. Fig. 4 shows the EI and FAB mass spectra for the product obtained under the latter conditions. Not only are the six adducts clearly seen, but those containing four, five and six addends also show that oxide derivatives (presumably as epoxides) are also present. The possibility that a second cyclopentadiene molecule undergoes cycloaddition with a cage addend may be discounted for two reasons; first, up to 12 equiv. of cyclopentadiene should add, secondly, the uptake of hydrogen would be less (there would be only one double bond present for each pair of cyclopentadienes that had added). Thus, if the six cyclopentadienes added as pairs the highest m/z value observed would be 1122, at variance with the experimental result; there would also be corresponding discrepancies at lower masses. By contrast, our proposal requires the highest m/z values to be 1128, cf. 1129 observed (the ^{13}C isotope effect causes the M + 1 peak to dominate in molecules containing more than ca. 80 carbon

atoms). Preferential addition to the cage rather than to the addend is consistent with the Diels–Alder reaction requirement of electron withdrawal in the dienophile, and the strong electron withdrawal by the fullerene cage.[6]

Further investigation of these reactions, together with isolation of the pure higher adducts (which may consist of both structural and geometric isomers), is in hand.

References

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