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Fluorine takes a hike: remarkable room-temperature rearrangement of the C_1 isomer of $C_{60}F_{36}$ into the C_3 isomer *via* a 1,3-fluorine shift

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In a toluene/$CDCl_3$ solution at room temperature, the C_1 isomer of $C_{60}F_{36}$ rearranges into the C_3 isomer over a period of four days, as a result of a unique 1,3-shift of fluorine; this rare example of addend migration across a fullerene cage surface is accelerated by air.

The possibility of addend migration across a fullerene cage has been of ongoing interest. Detection of such intramolecular rearrangements requires the presence of other addends as markers. Rearrangement of $C_{60}Br_6$ into $C_{60}Br_8$[1] and the lability of both $Pt(Et_2P)_2Pt$ groups,[2] and Vaska complex adducts[3] on [60]fullerene provided early examples. More recently, migration of anthracene from one π-bond to another in a $C_{60}F_{18}$:anthracene cycloadduct,[4] and of adducts during electrochemistry of bis-malonates,[5] have been reported.

We now report a definitive room-temperature rearrangement of the recently isolated and single-crystal X-ray characterised[6] C_1 isomer of $C_{60}F_{36}$ into a C_3 isomer in a solution of toluene/$CDCl_3$, under air. This occurred during acquisition of the ^{19}F NMR spectrum (toluene/$CDCl_3$) of the former, which is shown in Fig. 1(a). During a four day period, the 36-line spectrum slowly changed to give mainly the 12-line spectrum shown in Fig. 1(b), which is that of the C_3 isomer reported previously, Fig. 1(c)[7] together with a small amount of the unrearranged C_1 isomer. (N.B. ^{19}F NMR chemical shifts in the −(135–145) ppm region are very sensitive to solvent composition; thus for example, two of the peaks in this region for the C_3 isomer are seen to be give a double intensity coincident peak in Fig 1(b). On further standing the C_3/C_1 ratio of *ca.* 6 : 1 did not alter indicating that equilibrium between the isomers had been reached. If a similar solution was sealed under nitrogen, virtually no rearrangement occurred, pointing to the involvement of oxygen, possibly by inducing initial radical formation.

The structure of the C_3 isomer had been uncertain due to lack of coupling of adjacent fluorines in the ^{19}F NMR[8] but has now

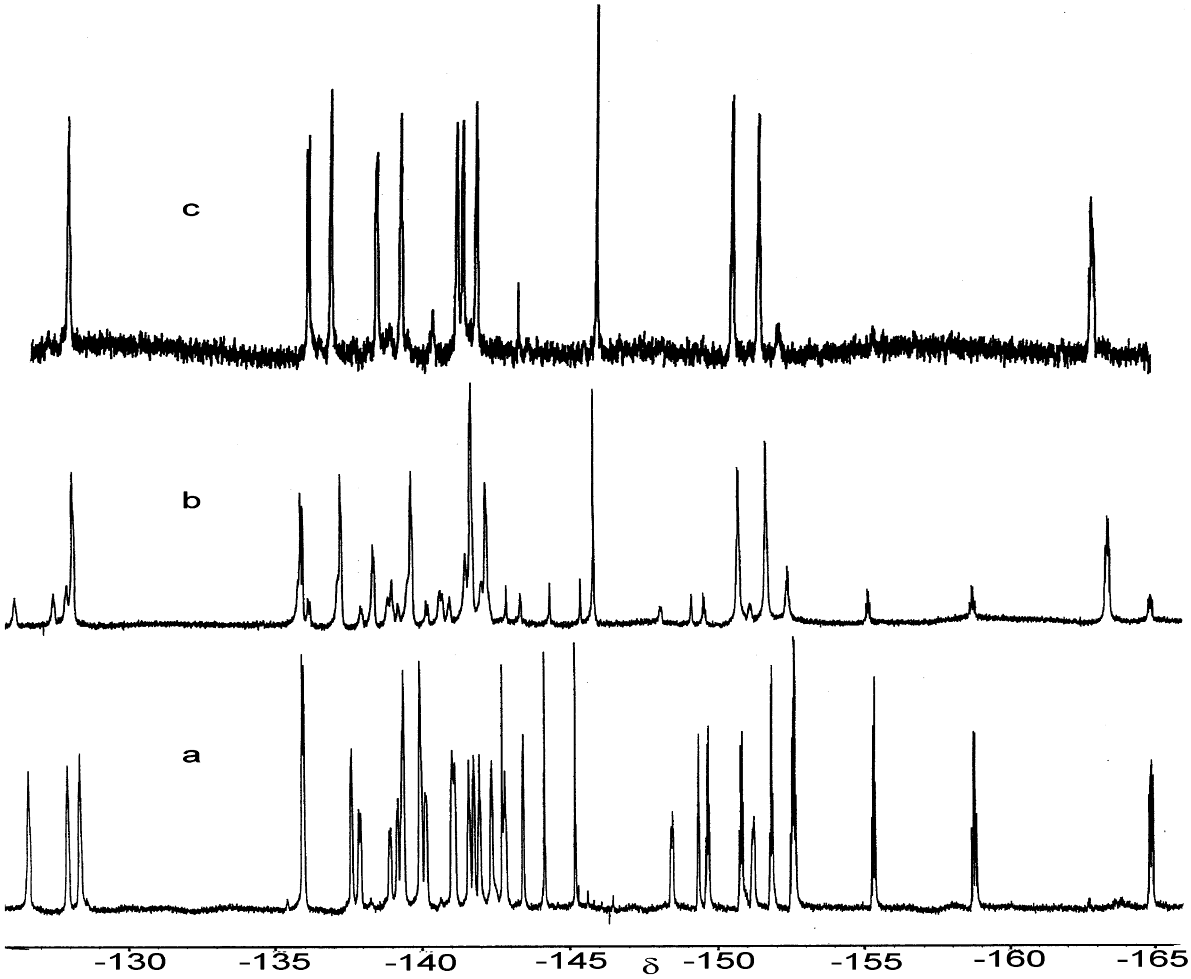

Fig. 1 ^{19}F NMR spectra of: (a) C_1-$C_{60}F_{36}$ initially; (b) after standing for four days; (c) pure C_3-$C_{60}F_{36}$.

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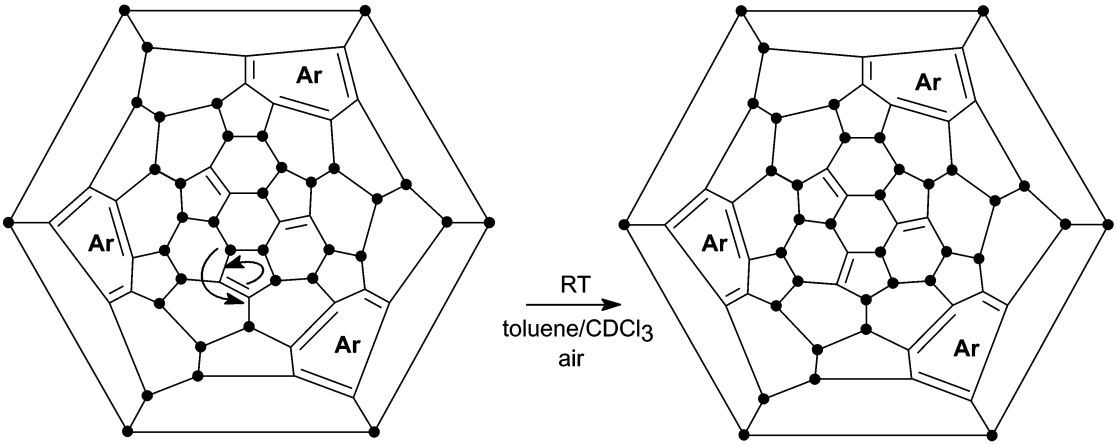

C_1 C_3

Fig. 2 Schlegel diagram of the C_1 and C_3 isomers of $C_{60}F_{36}$ (● = F) showing the 1,3-fluorine shift, which converts the former into the latter.

been clarified through the use of a higher sensitivity technique[9] and is shown in the Schlegel diagram (Fig. 2) along with that for the C_1 isomer. It can be seen that the only difference in the two structures is the location of one double bond, and the rearrangement evidently involves a simple 1,3-migration of a fluorine atom. As far as we are aware such a fluorine migration is unprecedented at room temperature, and it is likely (given the relatively non-polar nature of the solvent) that it migrates as $F^{\cdot}$ rather than F^-. To eliminate the possibility that rearrangement might occur *via* attack of F^- from traces of HF present, followed by bond migration and final F^- elimination,[10] we added both CsF and HF to a solution of the C_1 isomer and monitored the ^{19}F NMR spectrum. No acceleration of the rearrangement occurred, perhaps unsurprising given the low nucleophilicity of F^-.

Given the observed reaction, it might be expected that the C_3 isomer would rearrange further to the T isomer (*via* three 1,3-migrations of fluorine giving two intermediate C_1 isomers having one and two double bonds in the central hexagon). However, calculations (AM1)[11] indicate that these two intermediate structures will be 12.6 and 19.9 kcal mol^{-1} less stable than the C_3 isomer, and the process only becomes energetically favourable following the third migration (giving the T isomer which has a central benzenoid ring). Consequently rearrangement of the C_3 isomer into the T isomer is not expected and indeed, a solution of the C_3 isomer that was monitored during twelve weeks showed degradation due to hydrolysis, but no formation of the T isomer.[12]

Previously we had drawn attention to the fact that the pathway to formation of fluorinated fullerenes must involve some rearrangement of fluorines on the surface[6,7] since for example, the motif for $C_{60}F_{18}$ is found in the T isomer of $C_{60}F_{36}$ but not in the C_3 isomer, whilst the $C_{60}F_{36}$ motifs are not found in the structure for $C_{60}F_{48}$.[13] Moreover, fluorination of $C_{60}F_{36}$ with either F_2/NaF at 275 °C[14] or with K_2NiF_6 at *ca.* 500 °C[15] yielded $C_{60}F_{48}$ in each case. These reactions though involve very high temperature in contrast to the present reaction, which is exceptional in occurring at room temperature.

This rearrangement (coupled with the higher temperature of fluorination) may account for the failure to observe the C_1 isomer in a previous preparation of $C_{60}F_{36}$.[7] It provides yet another example of unique reactions that take place with fullerenes due to the unusual combination of electronic, steric and structural factors. In the present case the shift may befavoured by the very small perturbation of the structure that results from the rearrangement; the C_3 isomer is calculated to be only 1.6 kcal mol^{-1} more stable then the C_1 isomer.[6]

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