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The Remarkable Stable Emerald Green $C_{60}F_{15}[CBr(CO_2Et)_2]_3$: The First [60]Fullerene That Is also the First [18]Trannulene[**]

Xian-Wen Wei, Adam D. Darwish, Olga V. Boltalina, Peter B. Hitchcock, Joan M. Street, and Roger Taylor[*]

The fluorofullerene $C_{60}F_{18}$ is notable for having a fully delocalized and planar hexagonal ring and a normal curved "fullerene" region; it is also a hexa-substituted benzene.[1] Derivatives that have been made include oxides, which are produced by oxygen insertion into long FC–CF bonds (the first examples of oxahomofullerenes),[2] trifluoroalkyl derivatives produced by insertion of CF_2 groups into C–F bonds,[3] and a triphenyl derivative produced by nucleophilic substitution of three fluorine substituents by phenyl groups.[4]

Annulenes have long been of interest because of the question of whether the combination of $[4n+2]$ π-electrons and approximate planarity leads to aromaticity. A number of examples are now known in which this latter condition is indicated, notably by small differences in bond lengths (which usually range from 1.38 – 1.40 Å) in a cyclic chain comprising either sp^2 or sp/sp^2 carbon atoms.[5] The [18]annulenes have been of particular interest because of their presence in porphyrins, phthalocyanines, chlorophyll etc., and some have been prepared notably by Sondheimer et al., for example light brown plates of tridehydro[18]annulene.[6] In these compounds, the C–C bonds α to the double bonds are in either an *all-cis* or a *cis,trans* relationship. Very recently, the feasibility of annulenes having *all-trans* relationships ("trannulenes", which must have a hoop or barrel-like structure) has been

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[*] Dr. R. Taylor, Dr. X.-W. Wei, Dr. A. D. Darwish, Dr. P. B. Hitchcock
School of Chemistry, Physics & Environmental Sciences
Sussex University, Brighton BN1 9QJ (UK)
Fax: (+44) 1273-677-196
E-mail: R.Taylor@sussex.ac.uk

Dr. O. V. Boltalina
Chemistry Department, Moscow State University
Moscow 119899 (Russia)

J. M. Street
Chemistry Department, University of Southhampton
Southampton, SO17 1BJ (UK)

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conjectured.[7] We now report the isolation of the first trannulene that is also a fullerene.

Because $C_{60}F_{18}$ may be a useful precursor for the formation of donor–acceptor dyads with enhanced acceptor properties, we are carrying out a preliminary small-scale exploration of reactions that have been used for the formation of dyads derived from [60]fullerene itself. One notable reaction of this type introduced by Bingel's group involves deprotonation of an α-bromoester by sodium hydride. The resulting anion then attacks the cage to give, after loss of bromide, a substituted methanofullerene;[8] this reaction has been used very effectively for example in the fine work of Diederich et al. on tether-directed additions.[9] A very recent example showing the versatility of the reaction is given in ref. [10].

With the intention therefore of obtaining a methanofullerene from $C_{60}F_{18}$ we carried out the reaction with diethyl bromomalonate by using an excess of ester together with DBU; the latter improved base was introduced by Camps and Hirsch.[11] The reaction largely did not take place in the customary manner. The intermediate anion attacks the cage in the normal way, but instead of the bromide ion being lost, a fluoride ion is lost from a remote (δ) position. This results in either one, two, or three fluorine substituents being nucleophilically replaced by the $CBr(CO_2Et)_2$ moiety to give a mixture of mono-, di-, and trisubstituted derivatives (the relative extent can be controlled by the rate of addition of the base). We describe here the full characterization of the unique trisubstituted derivative $C_{60}F_{15}[CBr(CO_2Et)_2]_3$ (**1**) by ^1H and ^{19}F NMR spectroscopy, and by single-crystal X-ray crystallography.

The compound crystallizes as a toluene solvate giving emerald green diamond-shaped plates, and the single crystal X-ray structure is shown in Figure 1; for clarity the compound is shown as a Schlegel diagram (with two resonance structures) in Figure 2. The structure shows a number of most remarkable features:

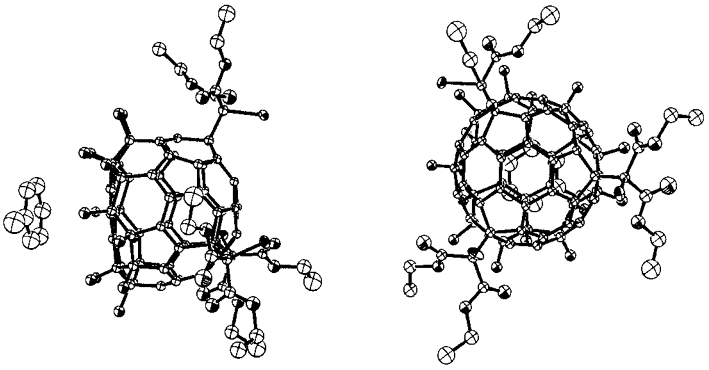


Figure 1. Two projections of $\mathbf{1}\cdot C_7H_8$ (ORTEP).

1. It is produced by a mechanism which is the first proven example of S_N2' substitution in a fullerene, a process we conjectured some years ago to account for the formation of epoxides on treatment of fluorofullerenes with moisture.[12] In the present instance substitution occurs at the δ position relative to the departing fluorine atom, as shown in Scheme 1. This is evidently favored over substitution at the alternative β position for steric reasons.

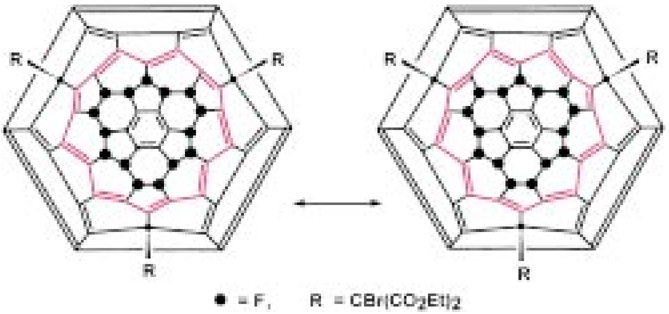
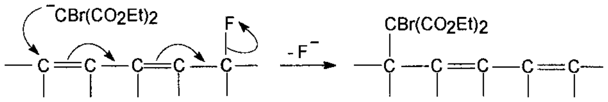


Figure 2. Schlegel diagrams for two canonical structures of **1** showing the resonance in the annulene belt.



Scheme 1. Mechanism of replacement of fluorine in $C_{60}F_{18}$ by $CBr(CO_2Et)_2$.

2. The molecule contains an equatorial 18π annulene belt of electrons. It is thus not only an aromatic fullerene because of the planar delocalized hexagon that is surrounded by fluorine atoms, but is also aromatic by virtue of the annulene belt of $[4n+2]$ π electrons (magenta-highlighted in Figure 2); the *all-trans* relationship of the constituent bonds of the belt defines this as a *trannulene.*
3. The electrons in this belt are highly delocalized as shown by the bond lengths for the constituent bonds (in bold, Table 1), which vary by a remarkably small 0.013 Å. By this measure, this belt comprises the most delocalized annulene of any kind yet found, and because of the size of the cage, the deviations from planarity are small and apparently not detrimental.

Table 1. Bond lengths [Å] in **1** (for notation, see Figure 3).

Bond	Length [Å]	Bond	Length [Å]
a	1.366	**j**	**1.397**
a′	1.378	k	1.468
b	1.484	l	1.530
c	1.608	m	1.428
d	1.565	n	1.376
e	1.655	p	1.539
f	1.490	q	1.420
g	1.506	r	1.402
h	**1.410**	s	1.448
i	**1.392**		

4. The high level of conjugation in the belt is responsible for the intense emerald green color. By contrast, the mono- and di-substituted compounds have only the pale yellow-green color characteristic of $C_{60}F_{18}$ and its derivatives, because the unsubstituted fluorine atoms prevent formation of an annulene belt.
5. The general structure may prove to be an outstanding candidate for investigation of donor–acceptor electronic interactions, through variation for example in the nature of the substituted alkyl addends. Such effects should for example be apparent from any observed color changes.

6. The hexagonal ring at the pole remote from the fluorine atoms has slightly enhanced aromaticity as shown by the bond length differences which are 0.046 Å compared to 0.060 Å for the corresponding hexagon in $C_{60}F_{18}$. This results from the presence of an sp^3 carbon atom in the adjacent pentagons which reduces strain and facilitates bond-shortening in the bond common to the hexagon.[13]
7. The molecule appears to be particularly stable, and shows no evidence for long-term degradation.
8. Compared to the corresponding bonds in the $C_{60}F_{18}$ precursor, bonds c, f, and h are shorter because of the reduced compression arising from the removal of adjacent fluorine atoms. By contrast, bonds l and p are lengthened because of the new adjacent addend.

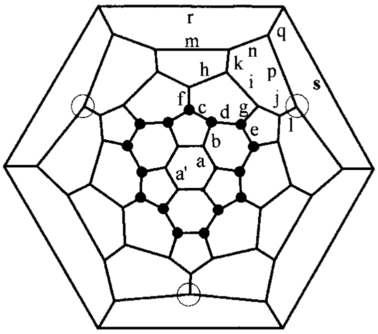


Figure 3. Schlegel diagram for **1** showing the notation for the symmetry-independent C–C bonds; ● = F, ○ = $CBr(CO_2Et)_2$.

The EI mass spectrum (70 eV) shows main fragmentation ions at $m/z = 1481$ and 1005 from loss of $CBr(CO_2Et)_2$ and $[CBr(CO_2Et)_2]_3$, respectively. A small peak at $m/z = 1639/1641$ results from the loss of one bromine atom from the parent molecule.

The ^1H NMR spectrum (Figure 4) comprises two resonances at $\delta_H = 4.13$ (q, $J(H,H) = 7.1$ Hz, 2H; CH_2), 1.038 (t, $J(H,H) = 7.1$ Hz, 3H; CH_3) showing the molecule to have C_{3v} symmetry. An unusual feature is that on lowering the temperature (see inset to Figure 4) the signals broaden and move downfield (run in $CS_2/CDCl_3$). This is not due to a chemical exchange process, but could indicate formation of a radical, and is to be investigated further.

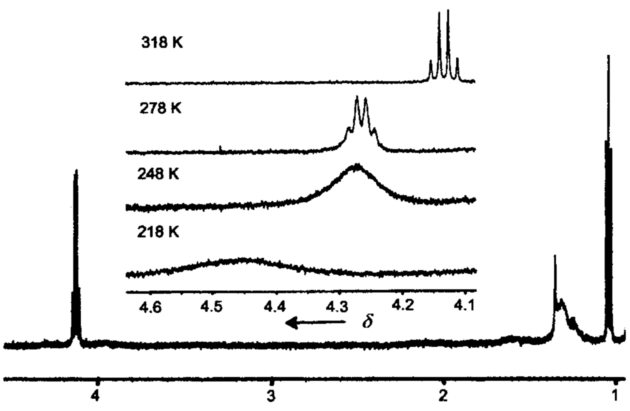


Figure 4. ^1H NMR spectrum (500 MHz, C_6D_6, 25 °C, TMS) of **1**.

The C_{3v} symmetry is confirmed by the ^{19}F NMR spectrum (Figure 5) comprising three coupled lines (2D spectrum, not shown) at $\delta_F = -136.72$ (1F), -143.87 (2F), -143.96 (2F). The notable difference in the spectrum from those for $C_{60}F_{18}$[1] (and its derivatives) is that the upfield line of these latter which arises from the fluorine atoms attached to the carbon atom surrounded by the less electronegative sp^3 carbon atoms is absent. This is consistent with the removal of the three outermost fluorine atoms.

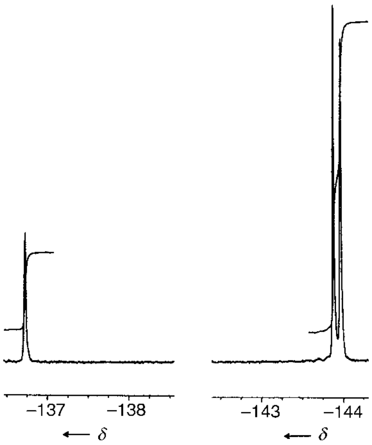


Figure 5. ^{19}F NMR spectrum (376 MHz, $CDCl_3$, 25 °C) of **1**.

The UV/Vis spectrum (Figure 6) shows bands at 368, 380, 389, 395, 400, 437, 612, and 658 nm, these latter pair accounting for the observed color. Further work is in hand to prepare related derivatives and to investigate their spectroscopic and other properties.

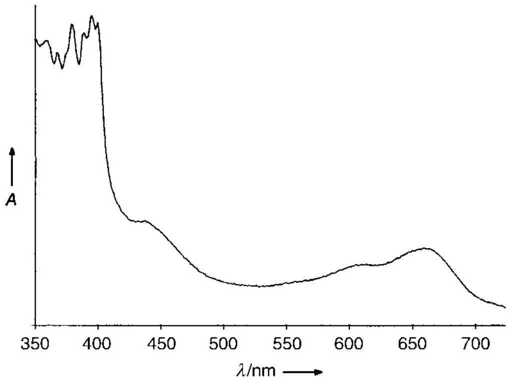


Figure 6. UV/Vis spectrum (hexane) of **1**.

Experimental Section

$C_{60}F_{18}$ (5 mg) was dissolved in toluene (15 mL) together with a slight molar excess of diethyl bromomalonate, and a ca. molar equivalent of DBU (dissolved in 0.4 mL of toluene) was added dropwise under argon. The solution turned green immediately and was stirred overnight at room temperature. A black precipitate was removed by filtration and the filtrate separated by HPLC (10 × 250 mm Cosmosil 5 Pye column, toluene elution at 4.7 $mL\,min^{-1}$). The fraction eluting at 3.55 min was repurified on a Cosmosil Buckprep column, (elution with 1:1 toluene:heptane at 4.7 $mL\,min^{-1}$) and **1** eluted at 5.0 min. The yield (ca. 30%) can be increased by using larger ester to DBU proportions to reduce the accompanying mono- and bis-substitution.

The structure was determined by mass spectrometry, ^{1}H and ^{19}F NMR spectroscopy as well as by X-ray diffraction.[14]

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Catalytic Enantioselective Addition of Nitro Compounds to Imines—A Simple Approach for the Synthesis of Optically Active β-Nitro-α-Amino Esters**

Nagatoshi Nishiwaki, Kristian Rahbek Knudsen, Kurt V. Gothelf, and Karl Anker Jørgensen*

The development of C–C bond-forming reactions that create two new stereogenic centers with high diastereo- and enantioselectivity in a single step can open new routes to highly valuable optically active compounds. The catalytic enantioselective addition to imines[1] belongs to this class of important reactions, and recently new catalytic asymmetric processes, for example, for Mannich-type,[2] ene,[3] allylation and alkylation,[4] aza-Diels–Alder,[5] Strecker,[6] and aromatic electrophilic substitution reactions[7] have appeared. Another important reaction of imines is the nitro-Mannich (aza-Henry) reaction, which is a powerful C–C bond-forming method that leads to 2-nitroamines.[8] To the best of our knowledge there is only one other paper that describes the catalytic enantioselective version of the nitro-Mannich reaction.[9] Although this reaction was catalyzed by a hetero-bimetallic complex, it has been described for nitromethane only and requires 60 mol% of the chiral ligand. In a very recent paper, we described the first catalytic asymmetric reaction of silyl nitronates with imines.[10] The reaction proceeds at $-100\,^\circ$C in the presence of bisoxazoline–copper catalysts to give 2-nitroamines with high enantioselectivities.

Herein we present a new and significantly simplified approach to the catalytic diastereo- and enantioselective nitro-Mannich reaction of an N-protected α-imino ester **1** with nitro compounds **2**. The reactions can be performed under ambient conditions to give β-nitro-α-amino esters **3** in good yields, and with high diastereo- and enantioselectivies [Eq. (1); Pg = protecting group].

(1)

1 **2** **3**

In the screening process, the reaction of N-(p-methoxyphenyl)-α-imino ester **1**[11] with nitropropane **2a** in the presence of NEt_3 as the base has been studied at room temperature by using different combinations of chiral ligands and Lewis acids (Scheme 1). The use of chiral bisoxazoline

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[*] K. A. Jørgensen, N. Nishiwaki, K. Rahbek Knudsen, K. V. Gothelf
Center for Metal-Catalyzed Reactions
Department of Chemistry, Aarhus University
8000 Aarhus C (Denmark)
Fax: (+45) 8619-6199
E-mail: kaj@chem.au.dk

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