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The Remarkable Chemistry of Trannulenes: Green Fluorinated Fullerenes with Unconventional Aromaticity

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In memory of Professor R. Taylor

Abstract: We report the first reaction of trannulenes involving their thermal isomerization to a new class of compounds termed "triumphenes". The thermodynamically controlled conversion of trannulenes into triumphenes is accompanied by an unprecedented migration of three organic addends from one hemisphere of the fullerene cage to another. The reaction products, bearing aliphatic substituents, might find applications in materials science as strong electron acceptors due to the presence of fifteen electron-withdrawing fluorine atoms in their molecular framework. It was revealed that the isomerization of trannulenes can be affected by the presence of unsaturated compounds in the reaction mixture. Heating of trannulenes $C_{60}F_{15}R_3$ with C_{60}, C_{70}, anthracene, or pentacene at reflux in 1,2-dichlorobenzene yields fluorinated derivatives $C_{60}F_{14}R_2A$, which possess a fused cyclic addend A. The products of this reaction have "triumphene-type" addition patterns and seem to be formed through an unprecedented sequence of elimination, addition, and isomerization steps. The molecular structure of a representative triumphene was proven unambiguously by X-ray single-crystal diffraction analysis and by NMR spectroscopy. The reactions revealed here open up numerous opportunities for chemical derivatization of fluorinated fullerenes. This method promises to provide a new path towards valuable photoactive materials and a new generation of fullerene-based compounds that are suitable for biomedical applications.

Keywords: annulenes · fluorine · fullerenes · isomerization

Introduction

Fullerene chemistry, since its birth in 1990, continues to excite the research community with the unusual chemical transformations of C_{60}, C_{70}, and their derivatives.[1] A number of reactions have been discovered that are specific for fullerenes and have no analogies in traditional organic chemistry.[2] Particularly, many generally irreversible reactions such as [2+1] cycloaddition of carbenes, nucleophilic cyclopropanation, and [2+3] cycloaddition of azomethine ylides become reversible with fullerenes.[3] This suggests that organic addends attached to the fullerene cages are quite labile. Another manifestation of such addend lability is a facile isomerization of some fullerene derivatives to the most thermodynamically stable structures under certain conditions. For instance, it was shown that fluorinated fullerenes and chlorofullerenes undergo numerous rearrangements under high-temperature conditions that dramatically change the position of addends on the fullerene cage.[4] Unprecedented room-temperature isomerization of the C_1 isomer of $C_{60}F_{36}$ to the more thermodynamically stable C_3 isomer proved that migration of a fluorine addend on the fullerene cage can occur readily.[4]

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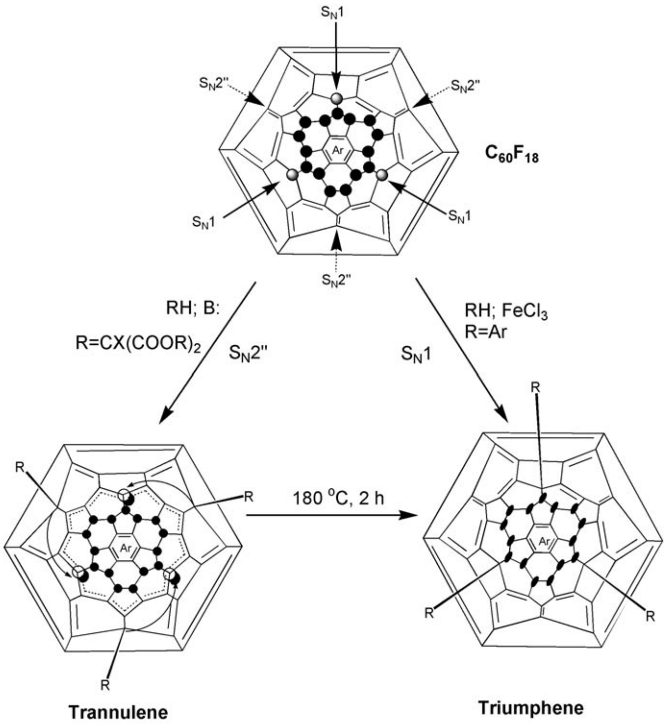
Such addend migration was also observed for other types of fullerene derivatives. Possible hydrogen migration around the fullerene cage in amine adducts $C_{60}(NR_2)_6H_6$ was first suggested in 1991;[5] however, this suggestion turned out to be incorrect.[6] Nevertheless, 12 years later it was proved that hydrogenation of fullerenes under drastic conditions is accompanied by a total migration of the attached hydrogen atoms on the cage to the most thermodynamically favorable sites to form specific products, such as $C_{60}H_{18}$ and three isomers of $C_{60}H_{36}$.[7] Some well-known examples include the thermal isomerization of open-cage fulleroids and azafullereroids to closed methanofullerenes and aziridinofullerenes, respectively;[1,2] the conversion of a solid C_{60}-anthracene adduct to the *trans*-1 isomer of the corresponding bisadduct and pristine C_{60};[8] the room-temperature migration of anthracene addends attached to $C_{60}F_{18}$; and some others.[9] Migration of a heterocyclic ring on the fullerene cage was observed recently for pyrrolidine derivatives of endohedral fullerene $Sc_3N@C_{80}$.[10]

Herein, we report a remarkable isomerization of trannulene fullerene derivatives $C_{60}F_{15}[CX(COOR)_2]_3$ (X = Br, COOR; R = Alkyl) to compounds named triumphenes through an unprecedented migration of three organic addends from one hemisphere of the fullerene cage to the other. This unusual transformation is illustrated in Scheme 1.



Scheme 1. Formation of trannulenes and triumphenes from parent $C_{60}F_{18}$ via S_N2'' and S_N1 reactions, respectively, and thermal isomerization of trannulenes to triumphenes.

Results and Discussion

Both types of compounds, trannulenes and triumphenes, are derived from the same fluorofullerene $C_{60}F_{18}$ precursor through substitution of three outlying fluorine atoms with organic groups. Lewis acid promoted reactions of $C_{60}F_{18}$ with aromatics proceed through an S_N1 mechanism; therefore, aromatic residues directly replace three fluorine atoms thus yielding triumphenes that have the same addition pattern as the parent $C_{60}F_{18}$.[11] In contrast, trannulenes have a very different addition pattern because their formation from $C_{60}F_{18}$ is operated by a rare S_N2'' mechanism in which the reacting nucleophiles (carbon anions $^-CX(COOR)_2$) become attached at the δ positions with respect to carbon atoms bearing the leaving fluorine atoms.[12] Such remote addition gives rise to the formation of a fully aromatic 18-membered *all-trans* annulene (trannulene) ring on the equator of the molecule that separates the fluorinated crown lying on one fullerene hemisphere from three organic addends attached to the other hemisphere. Trannulenes are unique compounds because they demonstrate nonclassical aromaticity. All eighteen π orbitals in trannulenes are overlapped both inside and outside the nonplanar aromatic trannulene ring. This distinguishes them from classical annulenes, which have their π orbitals overlapped above and below the planar aromatic rings (Figure 1).[13]

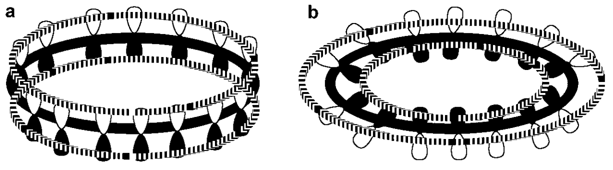
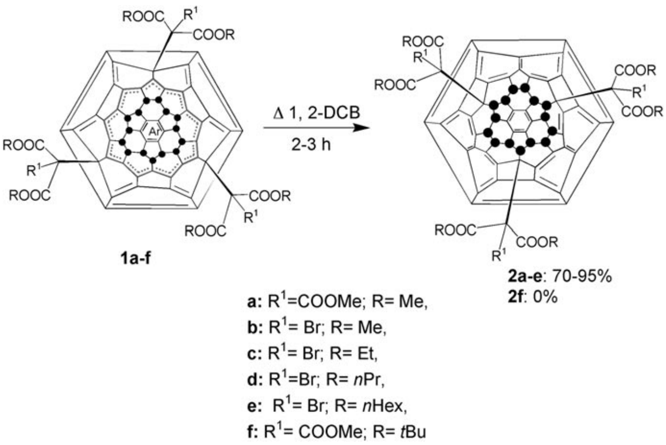


Figure 1. Schematic illustration of the p-orbital overlap in a) conventional aromatics and b) trannulenes.

The nonclassical nature of the aromaticity of trannulenes motivated a thorough investigation of these unusual compounds. Moreover, trannulenes have revealed some useful properties, for instance, their ability to efficiently harvest visible light, that might find many implementations, particularly in the design of solar-energy-converting devices and biomedicinal applications.[14]

To the best of our knowledge, we report herein the first reaction revealed for trannulenes. It was found that trannulenes **1a**–**e** (synthesized and spectroscopically characterized herein) undergo thermal isomerization to the corresponding triumphenes **2a**–**e** in 70–95 % yields (Scheme 2). The conversion of trannulenes into triumphenes is accompanied by a solution color change from emerald green (pure trannulene) to olive (a mixture of trannulene and triumphene) and then to yellow or orange (almost pure triumphene). Triumphenes are isostructural and isoelectronic to the parent fluorofullerene $C_{60}F_{18}$, therefore, they have lemon-yellow colors both in solution and in the solid state. The absorption spectra of $C_{60}F_{18}$ and representative examples of a triumphene and a trannulene are shown in Figure 2.



Scheme 2. Thermal isomerization of trannulenes **1a–e** to the corresponding triumphenes **2a–e**. 1,2-DCB = 1,2-dichlorobenzene.

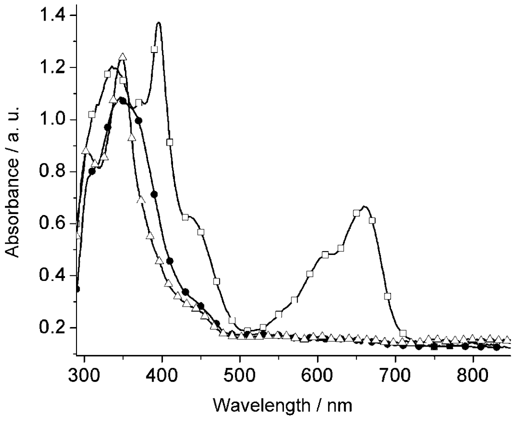


Figure 2. Absorption spectra of trannulene **1a** (□), triumphene **2a** (△), and $C_{60}F_{18}$ (●).

The molecular structures of the triumphenes that were formed from trannulenes were proven unambiguously by single-crystal X-ray diffraction data obtained for **2a**. Two projections of **2a** are shown in Figure 3. It can be seen from these drawings that three organic addends in **2a** are attached near the fluorinated belt to those carbon atoms that bear three outlying fluorine atoms in $C_{60}F_{18}$. Therefore, compound **2a** (and presumably **2b–e**) is the first triumphene that comprises three aliphatic organic addends, which distinguishes it from previously synthesized triumphenes with three aryl groups.[11] Thus, thermal isomerization of trannulenes can be considered to be a convenient synthetic route for the preparation of novel triumphenes with aliphatic substituents that cannot be obtained directly from fluorofullerene $C_{60}F_{18}$.

Another peculiarity of the structure of **2a** is that the −C(COOMe)$_3$ substituents are fixed in the crystal in a way that two COOR groups look towards the fluorinated belt and one COOR group looks towards the nonfluorinated hemisphere of the fullerene cage. Such orientation of the C(COOMe)$_3$ substituents is energetically the most preferable

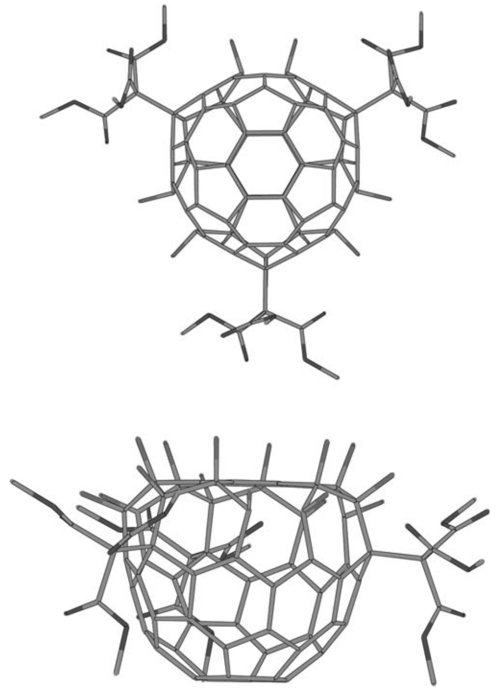
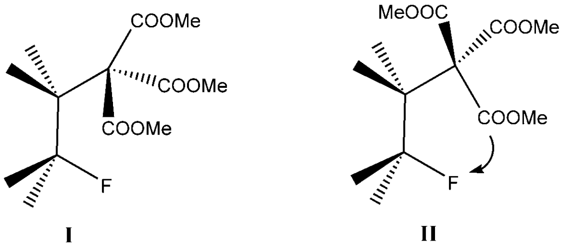


Figure 3. Two schematic projections of triumphene **2a** based on single-crystal X-ray diffraction data.

because, otherwise, there is an unfavorable eclipsed configuration with respect to the neighboring fluorine atom (Scheme 3). Therefore, conformation **I**, with minimized repulsion between the F and COOMe groups, is much more favorable than the very sterically strained conformation **II** (Scheme 3).



Scheme 3. Two possible conformations of the F−C−C−C(COOMe)$_3$ moiety with different arrangements of the C(COOMe)$_3$ group with respect to the adjacent fluorine atom. Drawing **I** corresponds to the minimal energy conformation identified from the single-crystal X-ray diffraction data; drawing **II** shows a conformation with unfavorable eclipsing interactions.

It has been shown that such orientation of the C(COOMe)$_3$ substituents is preserved in **2a** when it is dissolved in organic solvents. The NMR spectra of **2a** shown in Figure 4 proved that rotation of the C(COOMe)$_3$ substituents is completely frozen at room temperature. The appearance of two signals in the ^{1}H NMR spectrum with an integral ratio of 2:1 due to the COOMe protons, corresponds well to the same arrangement of C(COOMe)$_3$ groups ob-

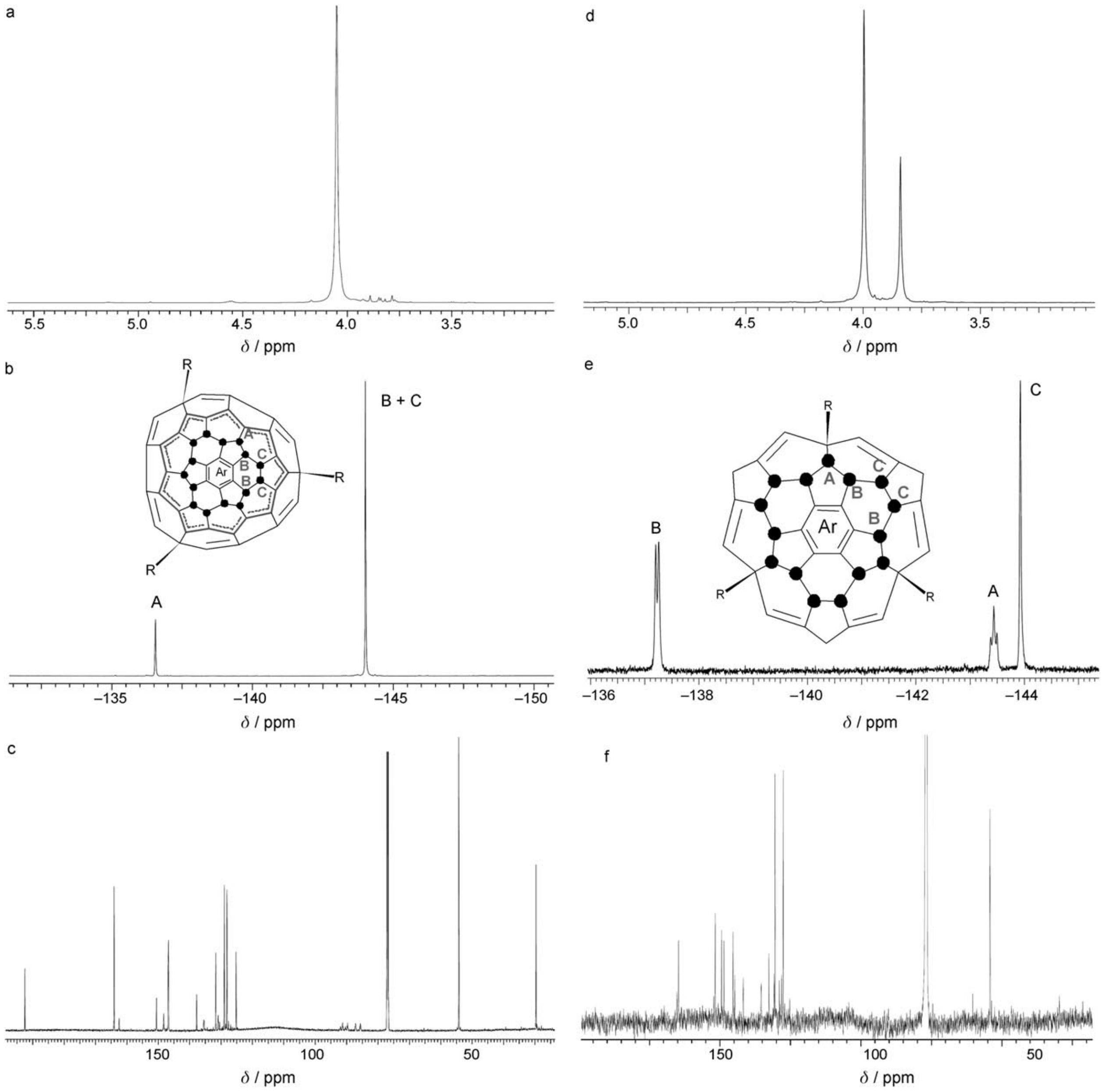


Figure 4. NMR spectra of trannulene **1a** (a–c) and triumphene **2a** (d–f): ^{1}H (a and d), ^{19}F (b and e), and ^{13}C NMR (c and f) spectra are shown.

served in the crystal structure. The ^{1}H NMR spectrum of **2a** showed no temperature dependence up to approximately 120 °C (measurements in C_6D_5Br), which suggests that the rotation barrier for $C(COOMe)_3$ substituents is unusually high. This high rotation barrier can again be explained by the strong steric repulsion between F and COOMe in conformation **II** shown in Scheme 3.

The restricted rotation with triumphenes **2c–e** greatly complicates their NMR spectra. Less symmetrical substituents, such as $CBr(COOAlk)_2$, make it possible for the coexistence of numerous isomers of **2c–e** that differ from each other by the respective orientations of the three $CBr(COOAlk)_2$ groups.

The NMR spectra obtained for **2b–e** were very similar and relatively complicated, thus suggesting the presence of more than one component in each sample. Indeed, the ^{13}C NMR spectra of **2d–e** revealed peaks characteristic for C_{3v} symmetrical triumphenes, such as **2a**, along with a large number (ca. 30–40 signals) of partially overlapped resonances that might be attributed to one or even two other isomers possessing low molecular symmetry. This reveals that thermodynamically controlled isomerization of **1b–e** to **2b–e** yields mixtures of several products that seem to be equally energetically favorable.

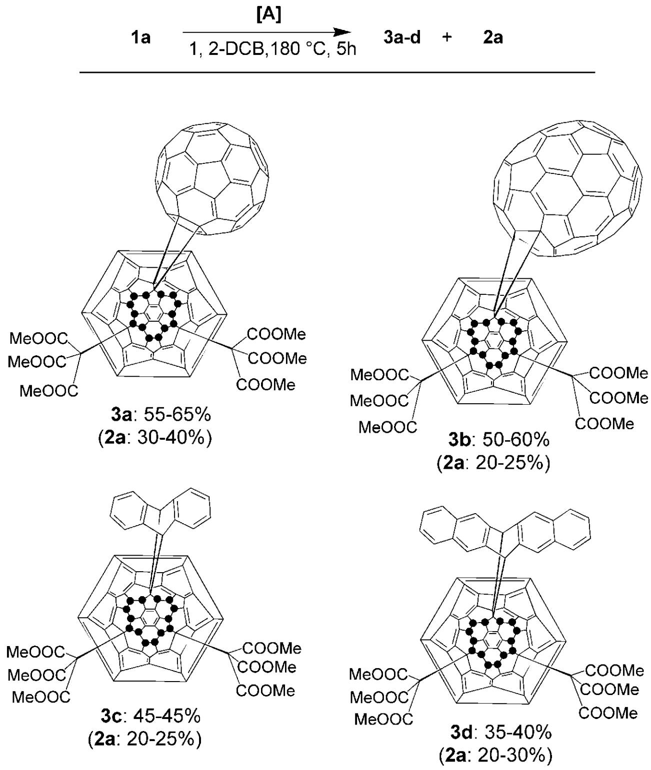
It is also notable that trannulenes **1a–f** undergo isomerization at different rates. Trannulene **1b**, which has the smallest organic groups, was the most reactive; in this case the isomerization was complete in 20 min. In contrast, trannulene **1f**, which has the most bulky and branched organic addends, did not isomerize even after 8 h. Prolonged heating resulted in degradation of **1f** with the formation of a complex mixture of products. Most probably, such degradation occurs as a consequence of thermal cleavage of the *tert*-butyl ester functions, followed by partial decarboxylation of the resultant acids. All attempts to isolate triumphene **2f** from a crude mixture of products formed from **1f** failed; most likely, this compound was not produced at all. The high reactivity of **1b** and the low reactivity of **1f** suggests that steric effects play an important role in this reaction. One can suspect that steric strain between the bulky −C(COOMe)(COO*t*Bu)$_2$ groups and neighboring fluorine atoms in **2f** is so strong that it makes this triumphene less stable than the corresponding trannulene **1f** and the reaction becomes thermodynamically unfavorable. In contrast, the relatively small size of the CBr(COOMe)$_2$ group leads to minimal steric repulsion in **2b**, therefore, it is rapidly formed during heating of **1b**.

Trannulenes were considered to be quite robust compounds due to the presence of an 18-membered aromatic ring, which stabilizes their structures significantly. Recently, we showed that trannulenes undergo rapid degradation under electrochemical and chemical reduction conditions.[15] Results reported herein prove that trannulenes (at least the compounds investigated herein) are less thermodynamically stable species than triumphenes. This finding leads to the conclusion that the formation of trannulenes from $C_{60}F_{18}$ is kinetically controlled, whereas the formation of triumphenes under Friedel–Crafts arylation of this fluorofullerene seems to be governed by thermodynamics.

Thermodynamically controlled conversion of trannulenes into triumphenes is accompanied by an unprecedented migration of three aliphatic substituents to δ positions on the fullerene cage. This migration might proceed through an intramolecular pathway, which means that organic groups really move along the sequence of single and double bonds from one hemisphere of the fullerene cage to another. Indeed, concerted, suprafacial, thermal 1,5-shift of the malonate groups is symmetry allowed. However, it is geometrically difficult to envisage because all of the conjugated C=C double bonds involved in the migration have *trans* configurations. Therefore, the rearrangement might involve a multistep series of concerted sigmatropic migrations that leads to the net 1,5-shift.

Another feasible alternative is a dissociation–readdition mechanism whereby the trannulene initially eliminates organic radicals or anions, which then reattach to the most thermodynamically favorable sites on the fullerene cage, thus forming the triumphene. We note that malonate radicals or anions could dissociate from this system in two ways: One would be as a free species independent of the fullerene counterpart, in which case they could be trapped by an appropriate radical or anion scavenger. The second way would produce a tightly bound radical or ion pair; in this case trapping would be inefficient. If the second process occurs, however, it would be indistinguishable from the intramolecular route discussed above.

To shed some light on the mechanism of trannulene isomerization, we attempted to isomerize **1a** in the presence of an excess of an unsaturated compound capable of scavenging $^{\bullet}C(COOMe)_3$ radicals or $^{-}C(COOMe)_3$ anions. Fullerene C_{60} is known to be an excellent radical sponge and a very active Michael acceptor. Therefore, it should efficiently scavenge both radicals and nucleophilic anions. Heating trannulene **1a** with a 10-fold molar excess of C_{60} produced compound **3a** ($C_{60}F_{14}R_2{=}C_{60}$) and the isomerization product **2a** with yields of 55–65 and 30–40%, respectively (Scheme 4). No other isolable byproducts were produced in this reaction. Moreover, when the reaction was conducted in the presence of a large excess of maleic anhydride, an even more powerful Michael acceptor than C_{60}, compound **2a** was afforded as the only isolable product with greater than 90% yield. These findings provide evidence that free radicals and anions are not involved as intermediates in the trannulene isomerization reaction.



Scheme 4. Isomerization of trannulenes in the presence of unsaturated compounds affords [2+2] and [2+4] adducts with triumphene-type addition patterns.

The isomerization of trannulenes to triumphenes might therefore proceed in an intramolecular manner and the organic addends should indeed move on the fullerene cage through a sequence of sigmatropic shifts. Alternatively, some tightly bound radical or ion pair could be formed upon dissociation of the trannulene and, following a readdition step, the malonate groups would be brought from one hemisphere of the fullerene cage to the other.[4] The precise mechanism for such addend migration remains unclear at the moment and additional studies are required to reveal further details.

The most striking result obtained in the experiments described above was the formation of compound **3a** under heating of **1** with C_{60}. Compound **3a** seems to be formed through an unprecedented cascade reaction involving elimination, addition, and isomerization, starting from trannulene **1a**. Further investigations revealed that the reaction has a general nature and that a number of related compounds ($C_{60}F_{14}R_2A$) can be obtained by treatment of the appropriate unsaturated molecules with trannulene **1a** in 1,2-dichlorobenzene when heated at reflux. In particular, we successfully prepared and characterized derivatives with fused moieties of fullerene C_{70} (**3b**), anthracene (**3c**), and pentacene (**3d**).

These reactions demonstrate an exceptionally high selectivity, suggesting that they are thermodynamically controlled. First, it was found that compound **3b** was formed as an individual isomer through addition of the fluorinated moiety $C_{60}F_{14}R_2$ across the 1,2-double bond (the 8,25-bond according to the new IUPAC nomenclature[16]) of the C_{70} cage. In contrast, most of the known reactions of C_{70} produce mixtures of products with 1,2-, 5,6-, and 19,20-addition pathways. The reaction of **1a** with pentacene involves only the central benzenoid ring of this fused aromatic molecule. However, it has been reported that the reaction of pentacene with C_{60} takes place across rings B and D and forms a dimeric product with two appended fullerene units.[17]

The purity of the isolated compounds **3a–b** was relatively high (>95%). Unfortunately, samples of compounds **3c–d** contained 7–15% impurities that could not be removed by using typical procedures. Nevertheless, the lower purity of **3c–d** did not prevent their spectroscopic characterization. Here we point out that all the fluorofullerene derivatives reported in this paper were isolated by using conventional column chromatography on silica; all of the previously reported fluorofullerenes and their derivatives were isolated and purified by using HPLC. In some cases even HPLC did not allow the respective authors to eliminate impurities or to separate mixtures of similar compounds.[18]

The molecular structures and compositions of the isolated compounds were confirmed by ^{1}H, ^{19}F, and ^{13}C NMR spectroscopy and by ESI mass spectrometry. The ^{19}F NMR spectra of compounds **3a–d** are shown in Figure 5; the ^{1}H and ^{13}C NMR spectra are provided in the Supporting Information. The NMR spectra show unambiguously that **3a–d** have C_s symmetrical molecular structures, whereas the ESI mass spectra prove that these compounds have molecular compositions $C_{60}F_{14}R_2=A$ (in which $R=C(COOMe)_3$ and A is an attached unit of C_{60}, C_{70}, anthracene, or pentacene); the obtained spectral data support the molecular structures of **3a–d** shown in Scheme 4. As additional proof, we note that the ^{19}F NMR spectrum of compound **3a** very closely resembles that of the previously prepared derivative $C_{60}F_{16}$N-MEM **4** (Scheme 5).[19] The same C_s symmetrical addition pattern as suggested here for **3a–d** was proven for aziridinofullerene **4** using 2D COSY ^{19}F–^{19}F NMR experiments. Furthermore, reaction of $C_{60}F_{18}$ with tetrathiafulvalene produced compound **5**, which has the same addition pattern as **3a–d** and **4**, although in this case the addend breaks the symmetry of the

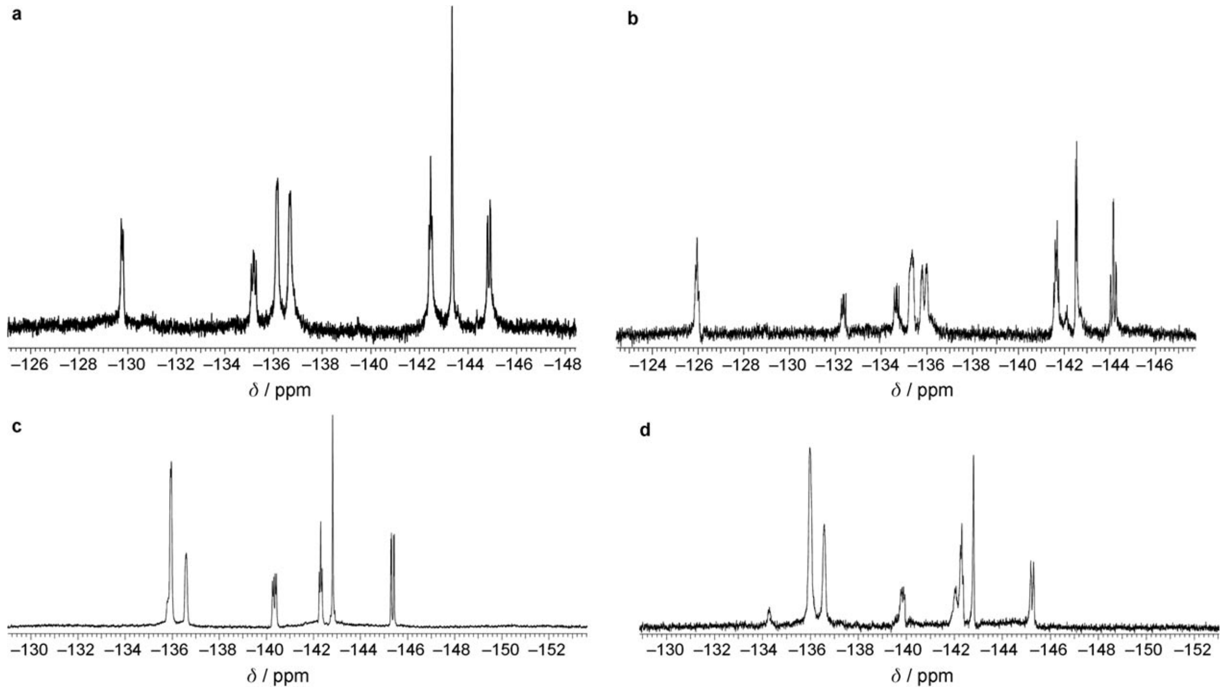
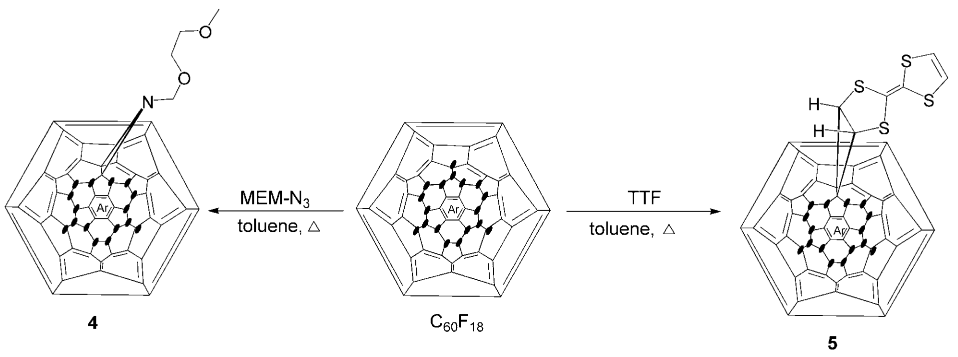


Figure 5. ^{19}F NMR spectra of a) **3a**, b) **3b**, c) **3c**, and d) **3d**.

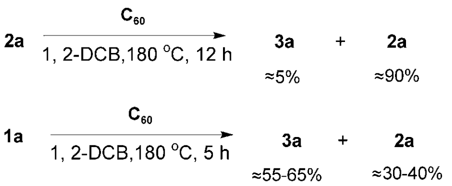


Scheme 5. Reactions of $C_{60}F_{18}$ with tetrathiafulvalene (TTF) and MEM-N_3.[19,20] MEM = methoxyethoxymethyl.

whole molecule to C_1 (Scheme 5).[20] The reaction pathway involving the replacement of neighboring fluorine atoms with a cyclic addend is thus well documented for $C_{60}F_{18}$.

The mechanism of formation of **3a–d** from **1a** and the corresponding unsaturated compounds (fullerenes, aromatics) is very intriguing. Most probably, it is based on a cascade reaction involving isomerization, elimination, and cycloaddition. However, the exact origin and the sequence of these stages remains unclear. We believe that the mechanism of formation of compounds **4** and **5** from $C_{60}F_{18}$ has some similarities to the conversion of **1a** into **3a–d**. Compounds **4** and **5** are derived from $C_{60}F_{18}$ by formal substitution of two neighboring fluorine atoms with a cyclic organic addend. It is quite probable that $C_{60}F_{16}$ is formed as an intermediate in this reaction. Reduction of $C_{60}F_{18}$ to $C_{60}F_{16}$ through fluorine transfer might be accomplished by using an excess of organic reagent (azide, tetrathiafulvalene) in an organic solvent.

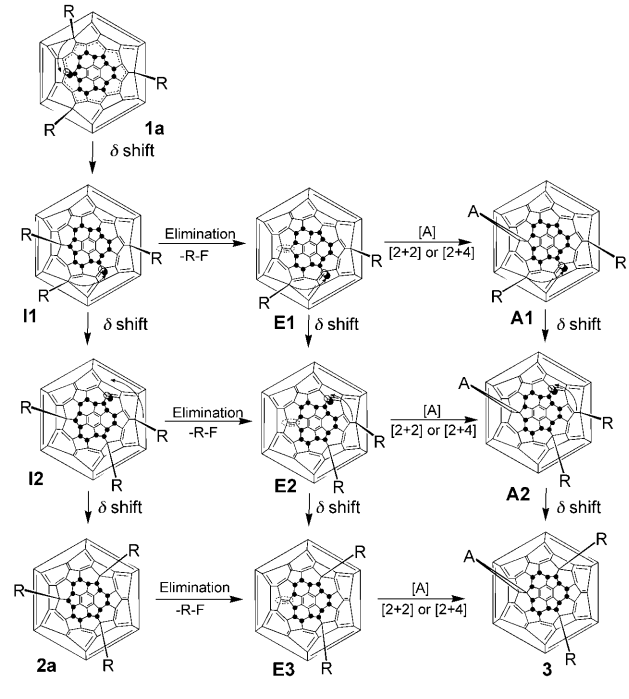
In the case of trannulene **1a**, one fluorine atom and one organic addend are formally removed from the $C_{60}F_{15}R_3$ precursor to form $C_{60}F_{14}R_2$=A as final product. By analogy with the chemistry of $C_{60}F_{18}$, triumphene **2a** might be considered to be a precursor that is converted into **3a–d** in the reactions with fullerenes and polycyclic aromatic hydrocarbons. If this is true, compound **2a** should be able to eliminate an organic radical ${}^{\bullet}R$ and a fluorine atom, perhaps together as R–F. To test this suggestion, we treated **2a** with C_{60} in 1,2-dichlorobenzene, which was heated at reflux for 12 h. Subsequent chromatographic separation of the reaction products resulted in approximately 90% recovery of **2a** and isolation of **3a** with around 5% yield (Scheme 6). This result revealed that **3a** can indeed be formed from **2a**. However, this reaction pathway does not predominate because the use of **1a** leads to much higher yields of **3a** than **2a**. Therefore, there has to be some other intermediate (or intermediates) formed from **1a** on the way to **3a** that is more active than the side product **2a**. In our opinion, it is very unlikely that trannulene **1a** first undergoes a [2+2] cycloaddition reaction with fullerenes, or a [2+4] cycloaddition reaction with anthracene or pentacene, forming $C_{60}F_{15}R_3$=A as an intermediate. Much more probable is the formation of $C_{60}F_{14}R_2$ as an intermediate, which then undergoes [2+2] or [2+4] cycloaddition reactions with the corresponding unsaturated counterparts.



Scheme 6. Reactions of **2a** and **1a** with C_{60} in 1,2-dichlorobenzene.

On the basis of such considerations, we can assume that **1a** undergoes three successive net δ shifts of the organic groups to afford the isomerization product **2a** (Scheme 7). These shifts might result either from a series of sigmatropic migrations or from addend elimination and following readdition through intermediate formation of a tightly bound radical or ion pair. These possible alternatives are discussed above. For the mechanism considered below, it is not important in which way malonate groups move to the δ positions on the fullerene cage.

The first net δ shift produces intermediate **I1**,which might be able to eliminate R–F to form **E1**. Migration of the next two organic addends (followed by elimination of R–F in



Scheme 7. Conjectured mechanism of the formation of adducts **3a–d** in the reactions of **1a** with fullerenes and polyacenes.

some cases) in a similar fashion affords **I2** and **E2**, and then **2a** and **E3**. We note that all three elimination products **E1**, **E2**, and **E3** have the same molecular composition ($C_{60}F_{14}R_2$) and can potentially undergo [2+2] and [2+4] cycloaddition reactions with fullerenes and aromatics, respectively. It is quite probable that **E1**, **E2**, and **E3** indeed react with unsaturated compounds, yielding **A1**, **A2**, and **3**, respectively. Following net δ shifts of the organic radicals R, compound **A1** can convert into **A2** and then into **3**. Therefore, each of the species **E1**–**E3** finally forms the title product **3**, although the three pathways do not seem to be equally efficient. Assuming that the conversions of **1a** into **I1**, **I1** into **I2**, and **I2** into **2a** are thermodynamically controlled, one can expect that the stability of these compounds increases in the order **1a**<**I1**<**I2**<**2a**. The same is most likely true for the series of elimination products, so that **E1** and **E2** are less stable and, therefore, more active than **E3** formed from **2a**. Therefore, the conversion of **1a** into **3** proceeds predominantly with the formation of **E1** and **E2** as intermediates. In particular, this conjecture explains why **3a** is formed much easier from **1a** (through **E1**–**E3**) than from **2a** (through **E3** only).

The considerations given above lead to the conclusion that **1a** affords compounds **3a**–**d** through sequences involving the following steps: 1) isomerization (initial one or two net δ shifts); 2) elimination of $FC(COOMe)_3$; 3) [2+2] or [2+4] cycloaddition, and 4) isomerization (final one or two net δ shifts). Subsequent studies will reveal more details of the mechanism of these unusual reactions.

Conclusion

We report the result of the first investigation into the chemistry of trannulenes, which are unusual fullerene derivatives that have been discovered recently.[12–14] We have revealed a very unusual migration of three aliphatic addends on the fullerene cage that enables the isomerization of trannulenes $C_{60}F_{15}R_3$ to the corresponding triumphenes. Such isomerization seems to proceed through three successive net δ shifts of three $CX(COOR)_2$ groups (proceeding either in an intramolecular manner or through tightly bound radical or ion pairs) and, to the best of our knowledge, this has no analogies in organic chemistry. Therefore, this reaction is quite interesting theoretically and deserves further investigation. Furthermore, thermal isomerization of trannulenes opens a route to the preparation of novel triumphenes with aliphatic substituents that might find valuable applications, for instance, as building blocks for light-sensitive, donor–acceptor ensembles.

The lability of the organic addends in trannulenes $C_{60}F_{15}R_3$ offers wide opportunities for chemical functionalization of the fluorinated fullerene core. In particular, trannulene **1a** was shown to yield unusual derivatives **3a**–**d** ($C_{60}F_{14}[C(COOMe)_3]_2{=}A$, in which A is a polycyclic addend) when heated together with unsaturated compounds such as fullerenes or polyaromatic compounds. These reactions are quite complex and proceed through unprecedented sequences of isomerization, addend elimination, and [2+2] or [2+4] cycloaddition steps. We note that the prepared compounds can be considered to be acceptor–acceptor (**3a**–**b**) and donor–acceptor (**3c**–**d**) dyads; the photophysical properties of these compounds are under investigation. The versatility of the developed method potentially allows for facile syntheses of numerous light-harvesting, donor–acceptor assembles that are attractive materials for solar-energy-conversion devices and nonlinear optics.

Experimental Section

Isomerization of trannulenes to triumphenes: Trannulene **1a**–**f** (0.03 mmol, 40–60 mg) was dissolved in anhydrous 1,2-dichlorobenzene (ca. 50 mL), and the solution was degassed and heated at reflux under an argon atmosphere for about 2 h (in the case of **1f** heating was extended to 14 h). The color of the reaction mixture changed during this time from emerald green to lemon yellow or yellow–orange (with the exception of **1f**, which afforded a dark-brown solution). Afterwards, the reaction mixture was cooled and purified by chromatography using a silica gel column. Typically, elution with toluene/ethyl acetate, 98:2 v/v yielded solutions of pure triumphenes **2a**–**e**, which were concentrated to dryness with a rotary evaporator. The resulting residues were washed with petroleum ether and dried in air to afford yellow solids of **2a**–**e** with 70–95 % yields.

Compound 2a: ^{1}H NMR ($CDCl_3$, 600 MHz): $\delta=3.84$ (s, 9H), 4.00 ppm (s, 18H); ^{19}F NMR ($CDCl_3$, 282 MHz): $\delta=137.40$ (d, $J=15.9$ Hz, 6F), 143.60 (t, $J=15.3$ Hz, 3F), 144.09 ppm (s, 6F); ^{13}C NMR ($CDCl_3$, 600 MHz): $\delta=29.6$ ($C(COOMe)_3$), 54.26 (OMe, two signals overlapped), 90.5 (m, CF), 92.1 (m, CF), 94.4 (m, CF), 96.3 (m, CF), 127.6, 128.2, 129.0, 130.5, 130.8, 132.7, 135.4, 135.5, 141.8, 144.8, 145.4, 148.6, 149.5, 151.7, 164.8 (C=O), 165.3 ppm (C=O).

Compound 2b: ^{1}H NMR ($CDCl_3$, 600 MHz): $\delta=3.81$ (s, 6H), 4.03 ppm (m, 12H); ^{19}F NMR ($CDCl_3$, 282 MHz): $\delta=135.34$ (m, 2F), 136.09 (m, 2F), 137.55 (m, 2F), 142.40 (m, 2F), 144.07 ppm (m, 7F); ^{13}C NMR ($CDCl_3$, 600 MHz): $\delta=55.15$ (OMe), 55.19 (OMe), 55.4 (OMe), 90.2 (br m, CF), 91.3 (br m, CF), 91.8 (br m, CF), 94.7 (br m, CF), 96.4 (br m, CF), 102.0 (br m, CF), 103.7 (br m, CF), 105.6 (br m, CF), 125.3, 127.02, 127.7, 128.2, 128.50, 128.54, 128.58, 128.62, 128.85, 128.97, 129.02, 129.4, 129.5, 129.8, 130.2, 130.7, 133.6, 134.5, 135.2, 135.3, 135.8, 136.4, 140.6, 140.8, 141.6, 141.8, 142.7, 144.74, 144.77, 144.82, 144.99, 145.02, 145.19, 145.20, 145.24, 145.27, 145.4, 145.5, 145.7, 145.8, 145.90, 145.96, 146.04, 146.6, 146.77, 146.82, 146.88, 146.95, 146.99, 147.11, 147.14, 147.2, 147.6, 147.71, 147.79, 147.86, 147.95, 148.06, 148.22, 148.26, 148.31, 148.35, 148.42, 148.5, 148.6, 148.83, 148.87, 148.91, 149.08, 149.13, 149.2, 149.3, 149.4, 150.26, 150.38, 150.44, 150.6, 151.26, 151.38, 151.45, 151.56, 151.61, 151.64, 151.7, 151.8, 151.9, 152.00, 152.1, 162.7, 165.2 (C=O), 165.5 (C=O), 165.60 (C=O), 165.62 (C=O), 165.65 ppm (C=O).

NMR spectra and spectral parameters for the other triumphenes synthesized and their parent trannulenes are given in the Supporting Information.

Synthesis of 3a–d from 1a: The syntheses were conducted following the typical isomerization procedure described above, except that 10 equiv of unsaturated compound (C_{60}, C_{70}, anthracene, or pentacene) were introduced per 1 equiv of **1a**. The isolation and purification of the products were performed by using conventional silica gel column chromatography with toluene/EtOAc mixtures as the eluent.

Compound 3a: ^{1}H NMR ($CDCl_3$, 600 MHz): $\delta=3.90$ (s, 3H), 3.93 (s, 3H), 4.05 (m, 3H), 4.07 (s, 3H), 4.08 (s, 3H), 4.24 ppm (m, 3H); ^{19}F NMR ($CDCl_3$, 282 MHz): $\delta=-129.98$ (d, $J=22.0$ Hz, 2F), -135.42 (dd, $^1J=33.1$, $^2J=23.3$ Hz, 2F), -136.36 (m, 2F), -136.90 (m, 2F), -142.69 (t, $J=18.1$ Hz, 2F), -143.55 (d, $J=3.24$ Hz, 2F), -145.08 ppm (dd, $^1J=33.1$, $^2J=5.83$ Hz, 2F); ^{13}C NMR ($CDCl_3$, 600 MHz): $\delta=33.5$ ($C(COOMe)_3$), 54.0 (OMe), 54.6 (OMe, two signals overlapped), 65.6 (cage sp^3), 66.9 (cage sp^3), 68.2 (cage sp^3), 128.8, 130.9, 132.5, 139.3, 140.4, 140.9, 141.4, 141.7, 142.0, 142.55, 142.59, 142.77, 142.80, 142.94, 142.97, 143.08, 143.10, 144.4, 144.8, 145.27, 145.35, 145.46, 145.54, 145.8, 145.9, 146.0, 146.17, 146.22, 146.3, 146.4, 147.3, 147.5, 148.3, 148.5, 148.9, 149.0, 149.14, 149.18, 149.20, 149.5, 149.8, 150.65, 150.67, 151.2, 151.53, 152.51, 162.7, 164.88, 164.94, 165.4, 167.8 ppm.

Spectral parameters for **3b–d** are given in the Supporting Information.

X-ray crystallography: Slow concentration of a solution of **2a** in chlorobenzene produced single crystals of **$2a\cdot 2C_6H_5Cl$** solvate that were suitable for performing X-ray diffraction analysis. Data collection from a crystal of **$2a\cdot 2C_6H_5Cl$** with dimensions 0.07×0.03×0.01 mm was performed with a MAR225 image plate at 100 K by using synchrotron radiation at the BESSY storage ring ($\lambda = 0.9050$ Å, BL 14.2, PSF of the Free University of Berlin, Germany). Structure solution and structure refinement were achieved with SHELXS97[21] and SHELXL97,[22] respectively. $C_{93}H_{42}Cl_2F_{15}O_{18}$; triclinic; $P\bar{1}$; $a = 16.2890(1)$ Å, $b = 18.9588(1)$ Å, $c = 22.6521(2)$ Å, $\alpha = 90.9596(4)°$, $\beta = 94.0701(4)°$, $\gamma = 93.3589(5)°$; $V = 6936.5(2)$ Å^3; $Z = 4$; $wR_2 = 0.251$ (for 25816 reflections and 2409 parameters); $R_1 = 0.094$ (for 18779 reflections with $I \geq 2\sigma(I)$). Two crystallographically independent fullerene molecules and four chlorobenzene solvent molecules were found. Some methoxy groups of the $C(COOMe)_3$ substituents, as well as two chlorobenzene molecules are orientationally disordered. CCDC-715951 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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