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Alleno-acetylenic scaffolding for the construction of axially chiral C₆₀ dimers

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ABSTRACT

The preparation of enantiopure dumbbell-type dimeric fullerenes consisting of two C₆₀ units connected by axially chiral alleno-acetylenic spacers is reported for the first time. As a key step, the attachment of the terminal alkyne moiety of the spacers to C₆₀ was efficiently accomplished by employing an *in situ* C₆₀-ethynylation methodology. In addition to spectral analyses, single-crystal X-ray crystallographic studies allowed for the unambiguous structural assignment of two C₆₀–alleno-acetylene conjugates. Circular dichroism measurements showed that the axial chirality of the allene moieties linked to the fullerene sphere is able to perturb the intrinsic symmetry of the fullerene π -system. Large characteristic Cotton effects were observed for two bisfullerenes in the 200–350 nm spectral region. UV/Vis absorption spectroscopic studies showed improved molar absorptivity of these dimeric fullerenes, but no strong evidence for a significant through-space electronic communication between the two C₆₀ spheres; electrochemical investigations further confirmed this conclusion.

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1. Introduction

Since their discovery in 1985¹ and their production on a preparative scale 5 years later,² fullerenes have attracted a great deal of attention.³ Among the various types of fullerene adducts, dimeric fullerenes have emerged as an intriguing class of molecules with remarkable electrochemical and photophysical properties.⁴ As such, a plethora of covalent fullerene dimers, endowed with different spacers between the fullerene units, have been reported in the literature,^{4,5} some of which exhibited enhanced performance as organic electronic materials for light harvesting,⁶ photo switches,⁷ charge separation,⁸ photovoltaic devices,⁹ and molecular qubits.¹⁰ However, although much is known about their synthesis and photophysical properties, some fundamental aspects, such as the perturbation of the π -system symmetry in the C₆₀ moieties by chiral spacers, as well as the electronic, through-space interaction between the spacer-connected carbon cages still remain to be properly addressed.

A weak, through-space electronic communication between C₆₀ moieties in organic bisfullerene derivatives has been observed only in few cases where the carbon spheres are either directly bonded to

each other or separated by a single atom spacer,^{11–16} whereas a stronger interaction has been observed by electrochemistry only through a metal cluster spacer in inorganic-based bisfullerenes (fullerene–metal sandwich complexes).^{17,18} The covalent bridging of fullerenes through conjugated organic spacers does not facilitate such an interaction either,¹⁹ since the attachment of C₆₀ to the spacer alters the hybridization of the fullerene bonding-C-atom from sp² to sp³, thus disrupting π -conjugation and hence the electronic communication between C₆₀ and spacer moieties. We envisaged that an appropriate choice of spacer could facilitate such a process and lead to well-defined interactions between the two fullerene moieties. To this end, and on the basis of molecular models, we selected a helically folded alleno-acetylenic spacer, in which helicity and conformational freedom could allow the two fullerene cages to be in close contact. We have previously shown that 1,3-di-*tert*-butyl-1,3-diethynylallenes (DEAs; e.g., (P)-(+)–1, Fig. 1a)^{20,21} are stable chiral building blocks for the construction of acyclic alleno-acetylenic oligomers ((P)₂-(+)–2–(P)₁₆-(+)–5, Fig. 1b), which exhibited exceptionally strong chiroptical properties as a result of their helically folded secondary structure.²² Thus, the objective of the present study was not only to explore the potential of alleno-acetylenic architecture in the construction of novel, helically folded spacers for dumbbell-type fullerene dimers that could facilitate through-space interaction between the two terminal C₆₀ moieties without perturbing their π -systems at their proximal

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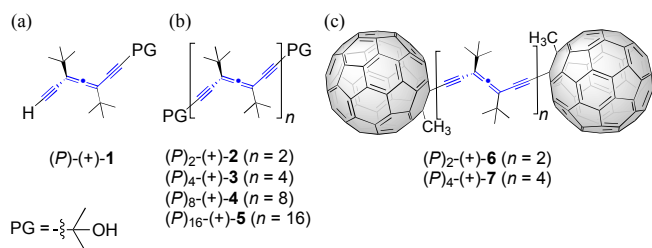


Fig. 1. (a) Optically active 1,3-di-*tert*-butyl-1,3-diethynyllallene (DEA) used in our previous studies^{20,21} for the construction of (b) enantiopure alleno-acetylenic oligomers,²² and in the present study for the construction of the enantiomers of (c) fullerene dimers endowed with bis- or tetrakis-DEA spacers. PG=protecting group. For the sake of simplicity, only the (P)-configured enantiomers are shown.

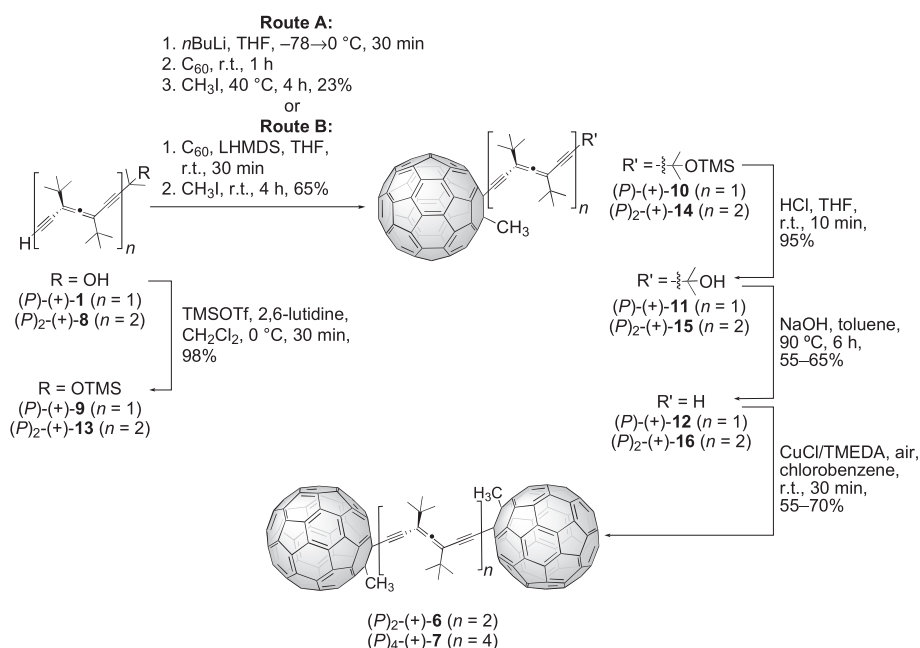
areas, but also to investigate the influence of the axially chiral spacer on the electronic properties of the resulting C₆₀–allenoacetylene–C₆₀ dimers ((P)₂-(+)-6 and (P)₄-(+)-7, Fig. 1c; for the sake of simplicity, only the (P)-configured enantiomers are shown). It is essential to mention here that surprisingly, and despite the considerable ongoing research on chiral fullerene derivatives for applications in materials science and medicinal chemistry,^{23,24} the preparation of chiral fullerene dimers has been largely neglected.²⁵

2. Results and discussion

For the purpose of the present study, we prepared two enantiopure bisfullerenes (P)₂-(+)-6 and (P)₄-(+)-7 endowed with a bis- or tetrakis-DEA spacer, respectively.

Scheme 1 outlines only the synthesis of the (P)-configured dimeric fullerenes; the (M)-enantiomers were obtained in an equivalent way, starting from (M)-(-)-1 and (M)₂-(+)-8, respectively. Enantiopure 1,3-DEA (P)-(+)-1 was accessed in multi-gram quantities from commercially available pivaloyl chloride in 40% overall yield using a previously reported four-step synthetic protocol, followed by enantiomeric resolution by HPLC on a chiral stationary phase.^{21,26} The tertiary hydroxyl group of alcohol (P)-(+)-1 was protected as TMS ether by treating with TMSOTf and 2,6-lutidine in

CH₂Cl₂ at 0 °C to give (P)-(+)-9. Subsequently, in the key step of this synthesis, terminal alkyne (P)-(+)-9 was reacted with C₆₀ to afford 1-allenoethynyl-2-methyl[60]fullerene (P)-(+)-10. To this purpose, we initially followed a well-established, general method for the ethynylation of fullerenes, namely the lithium acetylide nucleophilic addition to C₆₀, in which lithium acetylides are first generated with *n*-BuLi or *t*-BuLi and then transferred into a slurry of fullerene in THF under inert atmosphere.^{19a,27} This methodology has previously enabled the addition of several alkynes to C₆₀ in moderate yields, with the addition of TMS–acetylene being one of the most prominent examples.^{19b,c,28,29} Indeed, in the present case, the nucleophilic addition of the corresponding lithium acetylide derived from (P)-(+)-9 to C₆₀, followed by quenching with excess iodomethane, furnished (P)-(+)-10 in 23% yield (Scheme 1, Route A). Also, consistent with previous reports, it was observed that the yield of this reaction is highly dependent on the reaction conditions, particularly on the effective exclusion of O₂ and moisture from the reaction mixture and the efficiency of stirring during the slow addition of the acetylide to C₆₀.²⁷ Later, in an attempt to improve the reproducibility and overall efficacy in the synthesis of (P)-(+)-10, we found out that the yield could be substantially increased by adapting the *in situ* C₆₀-ethynylation conditions first reported by Tour and co-workers.^{30,31} Accordingly, (P)-(+)-9 and C₆₀ were added in THF and sonicated under argon atmosphere for 3 h before 4 equiv of lithium hexamethyldisilazide (LHMDS) was added; subsequent quenching with excess iodomethane afforded (P)-(+)-10 in 65% yield (Scheme 1, Route B). A two-step, sequential removal of the trimethylsilyl (→(P)-(+)-11) and the 2-hydroxy-2-propyl protecting groups afforded the key building block (P)-(+)-12—a C₆₀-substituted terminal acetylene—in 50% overall yield. Finally, (P)-(+)-12 was subjected to oxidative homocoupling under standard Hay conditions in chlorobenzene to furnish dumbbell (P)₂-(+)-6 with the bis-DEA spacer in 70% yield. The synthesis of the enantiomerically pure bisfullerenes (P)₄-(+)-7 and (M)₄-(+)-7 with a longer, tetrakis-DEA spacer was accomplished in an analogous fashion to that described above, starting from (P)₂-(+)-8—via the intermediacy of (P)₂-(+)-13, (P)₂-(+)-14, (P)₂-(+)-15, and (P)₂-(+)-16—or from (M)₂-(+)-8, respectively (Scheme 1; for further details, see Experimental section).



Scheme 1. Synthesis of enantiopure C₆₀ dimers (P)₂-(+)-6 and (P)₄-(+)-7. TMSOTf=trimethylsilyl trifluoromethanesulfonate, LHMDS=lithium hexamethyldisilazide, THF=tetrahydrofuran, TMEDA=*N,N,N',N'*-tetramethylethylenediamine.

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