Two new types of π-conjugation between a fullerene sphere and an addend†

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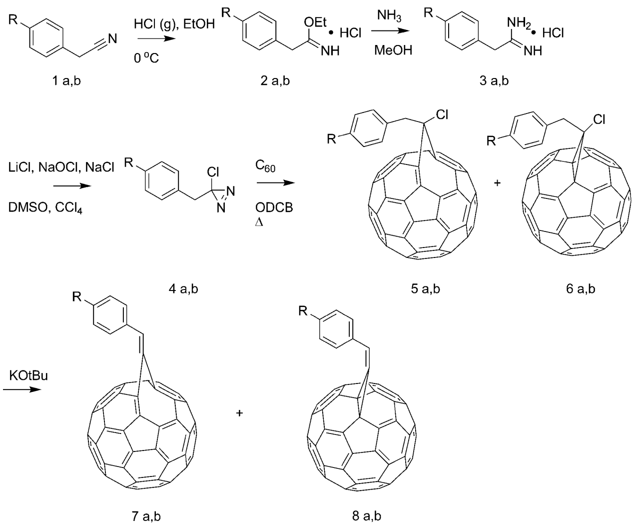
Diazirine addition reactions to C_{60}, followed by an HCl elimination step, yielded [6,6] and [5,6] sp^2 carbon bridged fullerenes. The [5,6] adducts (alkylidenehomofullerenes) are the first examples of fullerene structures where the addend is attached to the fullerene cage in a true, albeit highly bent, alternating single–double bond fashion.

Since Krätschmer *et al.* first isolated C_{60},[1] fullerenes have found many applications in molecular electronics. Their unique electron accepting and electron conducting properties have rendered them very useful for applications in organic photovoltaic devices.[2–5] Over the years many synthetic methodologies have been developed to functionalize fullerenes.[6–9] The solubility and processability of fullerenes can be perfectly tuned for the various applications in this way. Altering the electronic properties of fullerenes by direct interaction with addends has been more challenging so far. Yet such tunability is desired, since the ability to optimize the electronic properties of molecular components is essential in the field of molecular electronics. Wudl and co-workers found a moderate interaction between the addend π-system and the fullerene moiety in certain spiroannelated methanofullerenes.[10] This 'periconjugation' results from the overlap between the addend p_z orbitals, which are aligned in a perpendicular way to the nearby fullerene orbitals, in contrast to spiroconjugation, where the interacting orbitals are oriented in one plane.[11] In the periconjugated construct there is an electronic overlap between two π-systems, separated by two sp^3 carbons. We have shown that placing electron donating and withdrawing groups on the phenyl ring of PCBM (phenyl-C_{61}-butyric acid methyl ester) results in modest variations of the fullerene LUMO level, through an inductive through-bond effect.[12] For all of the above mentioned approaches, in which there is relatively weak electronic coupling, there is a strict limit for the electron donating power of the addend, because when energetically feasible, the compound becomes a donor–acceptor dyad. In that case, the compound does not function as a normal electron acceptor anymore, especially not under illumination because intramolecular photoinduced electron transfer will become a competing process.

In order to obtain the strongest possible electronic coupling, (linear) π-conjugation between two moieties leading to push–pull systems is, normally, optimal. With fullerenes, this has never been achieved for a good reason: it is impossible to make a tangential type of linearly conjugated addend, unless a substantial part of the fullerene cage is broken. The closest possible approximation of an attachment point for a 'linearly' conjugated addend to an intact fullerene is an open [5,6] sp^2 carbon bridged fullerene, as in alkylidenehomofullerene **7** (Scheme 1). Albeit close to orthogonal because the addend cannot be tangentially attached, the π-system connecting the fullerene with the addend in **7** is made up of alternating single and double C–C bonds. In the isomeric stucture **8**, an alkylidenecyclopropafullerene, one sp^3 carbon separates the two π-systems, that can now interact in a way somewhat similar to the periconjugation configuration, but with quite different symmetry. The first method of synthesizing both types of structures is reported below.

We took diazirines as precursors for the fullerene addition reaction. Diazirines decay under photolytic or thermolytic conditions with expulsion of nitrogen. Two interesting intermediate species are formed during this decay: a carbene species and a diazo species. In order to study this decay pathway, Nagase *et al.* used C_{60} as a mechanistic trap. Carbene species react with C_{60} to form [6,6] adducts. Diazo intermediates, on the other hand, form [5,6] adducts.[13] When 3-chloro-3-alkyldiazirines were used, both the [6,6] and the [5,6] adduct were obtained, with the chlorine atom at the cyclopropane.[14] The substituent on the diazirine ring determined the ratio of [5,6] and [6,6] addition product.[15] We envisioned 3-chloro-3-phenyldiazirines as candidates for addition reactions to C_{60}.



Scheme 1 Synthetic overview ((a) R = H, (b) R = NO_2).

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Table 1 UV-Vis absorption data of the fullerene derivatives

Compound	Absorption/nm	Red shift/nm
5a	537, 602 (sh)	11
7a	548, 603 (sh), 664 (sh)	
5b	540, 603 (sh)	7
7b	547	
6a	497	18
8a	515	
6b	490	21
8b	511	

Subsequent HCl elimination would then lead to an exocyclic C=C bond on the [5,6]-bridge or on the [6,6]-cyclopropane ring, respectively (Scheme 1).

The diazirine approach allows for the presence of the leaving group (here Cl^-), necessary for β-elimination. Alternative precursors for diazo compounds, *e.g.* hydrazones,[9] do not allow this. In the case of the [6,6] adduct, the exocyclic C=C bond is positioned for a peri-type conjugation with the fullerene π-system. In the case of the [5,6] adduct, the exocyclic C=C bond is connected to the fullerene π-system in the desired alternating single–double bond fashion. Substituting the phenyl ring with electron donating or withdrawing groups would further allow the determination of the electronic coupling in this 'bent conjugated' system.

[5,6]-Adducts **7a** and **7b** and [6,6] adducts **8a** and **8b** were synthesized *via* this diazirine route (see Scheme 1). The diazirines **4a** and **4b** were prepared according to literature procedures.[16,17] The reaction with C_{60}, performed at 60 °C, was stopped after 50% conversion (C_{60} 50%, [6,6] 35%, [5,6] 5%). The [5,6] and [6,6] adducts were separated by preparative HPLC. Subsequently, each of the isomers was subjected to HCl elimination. Acceptable results were obtained using KOtBu in ODCB (see Scheme 1). Nevertheless, the yield of the desired elimination products from [5,6] adducts **5a** and **5b** was extremely low. Hence, while **8a**, **b** could be fully characterized, the [5,6] homofullerenes **7a** and **7b** could only be investigated using LC-MS and UV-Vis spectroscopy. In all cases, after performing the elimination step, MS traces showed a mass 36 m/z lower than for their precursor fullerenes, clearly indicating the elimination of HCl. The UV/Vis absorption spectra are indicative of the extent of electronic coupling in the elimination products. In the case of the [6,6] isomers, a red shift of 18 nm (for **8a**) and 21 nm (for **8b**) was observed in the 500 nm region (see Table 1). The [5,6] isomers showed only a slight red shift (11 nm and 7 nm for **7a** and **7b**, respectively) in the 540 nm region. Furthermore a new absorption at 664 nm, probably caused by a previously forbidden π–π* transition, was observed for compound **7a**. Interestingly, the optical bandgap and the first reduction potential of **8a** were found to be very close to those of a normal methano[60]fullerene.[18] Hence, the interaction between the fullerene and the addend in **8a** appears to happen mainly in orbitals other than the HOMO and LUMO.

The observed shifts for the [6,6] adducts are attributed to a rather effective periconjugation between both π-systems. The effect is most likely due to the close proximity of both π-systems. Note that in compound **9**, synthesized by the Wudl group, both π-systems are separated by two sp^3 carbon atoms, while in the case of **8a** both π-systems are separated by only one sp^3 carbon atom. Besides being in closer proximity, the p orbitals are oriented differently (by 90°) in both compounds.

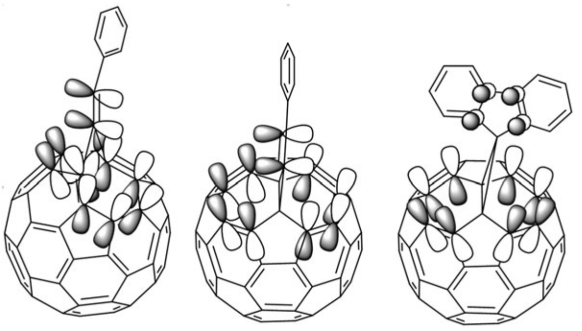

Fig. 1 Possible p orbital overlap of compounds **7a**, **8a** and **9**, with different orbital symmetries chosen for maximal overlap.

The overlap of the alkene p orbitals and the fullerene p orbitals in compounds **8a** and **8b** is stronger than the overlap of the phenyl p orbitals and the fullerene p orbitals in compound **9** (see Fig. 1). Furthermore, the orbital symmetry of the fullerene part is quite different in **8** and **9**. This likely explains the observed differences between the two types of periconjugated systems.

In conclusion, two new types of π-conjugated fullerene–addend linkages have been realized. The new type of periconjugation, as present in the [6,6] adducts, is quite effective. The observed red shift in the [5,6] homofullerenes is smaller than the ones observed in the corresponding [6,6] adducts. Hence, the strongly bent 'linear' π-conjugated system in the [5,6] adducts (*e.g.* **7a** in Fig. 1) functions as a slightly weaker electronic coupler. Because the neighbouring p orbitals on the bridge and the bridgehead sp^2 carbon atoms are almost orthogonal in the [5,6] adducts, it seems more adequate to regard this system as periconjugated as well. The fullerene–addend interaction might be improved using an addend with a better energy match with respect to the fullerene core. This will be the subject of future research.

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18 PCBM: $E_g = 1.73$ eV; $E_{1/2}{}^1 = -1.078$ V. **6a**: $E_{1/2}{}^1 = -1.047$ V. **8a**: $E_g = 1.74$ eV; $E_{1/2}{}^1 = -1.033$ V (*vs.* Fe/Fe$^+$).