ORGANIC
LETTERS

2007
Vol. 9, No. 15
2943−2946

Synthesis of Homoconjugated Oligomers Derived from 7,7-Diphenylnorbornane

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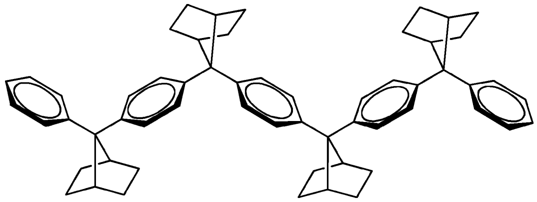
Received May 18, 2007

ABSTRACT



Cofacial aryl rings = extended homoconjugation

A methodology for the synthesis of monodisperse homoconjugated oligomers (dimer, trimer, and tetramer) derived from cofacial 7,7-diphenylnorbornane (DPN) is described. Extended aromatic homoconjugation is observed in these oligomers as revealed by the electronic spectra. The effective homoconjugation length (EHL) is in the range of 4–5 DPN subunits.

Monodisperse conjugated oligomers are currently of great interest because of their applications in molecular electronics and optoelectronics due to their properties such as electrical conductivity, electroluminescence, and nonlinear optical properties.[1] These organic bridges also play an important role in studies directed to the understanding of photoinduced electron- and energy-transfer processes.[2] Modulation of the electronic and optical properties as well as of the applications of molecular wires can be achieved by using alternative modes of electron delocalization, such as cross-conjugation,[3] spiro-conjugation,[4] toroidal-conjugation,[5] π-stacking,[6] and homoconjugation.[7]

Until now, very few examples of electron delocalization in polymers and oligomers by aromatic homoconjugation have been reported. In a previous work,[7] we described the first example of a soluble polymer with alternating conjugation−homoconjugation in which homoconjugated segments were 7,7-diphenylnorbornane (DPN) subunits. In DPN, aryl rings adopt a cofacial conformation forced by the norbornane framework.[8] Now we report the synthesis and characteristics of new homoconjugated molecular wires derived from DPN (**10**). The preparation of these oligomers is shown in Schemes

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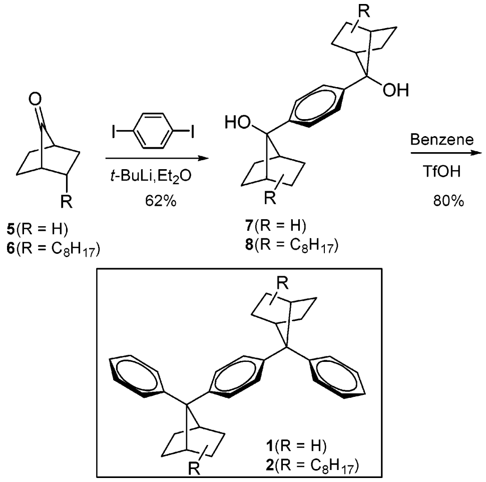
10.1021/ol071161b CCC: $37.00

Scheme 1. Synthesis of DFN Dimers **1** and **2**

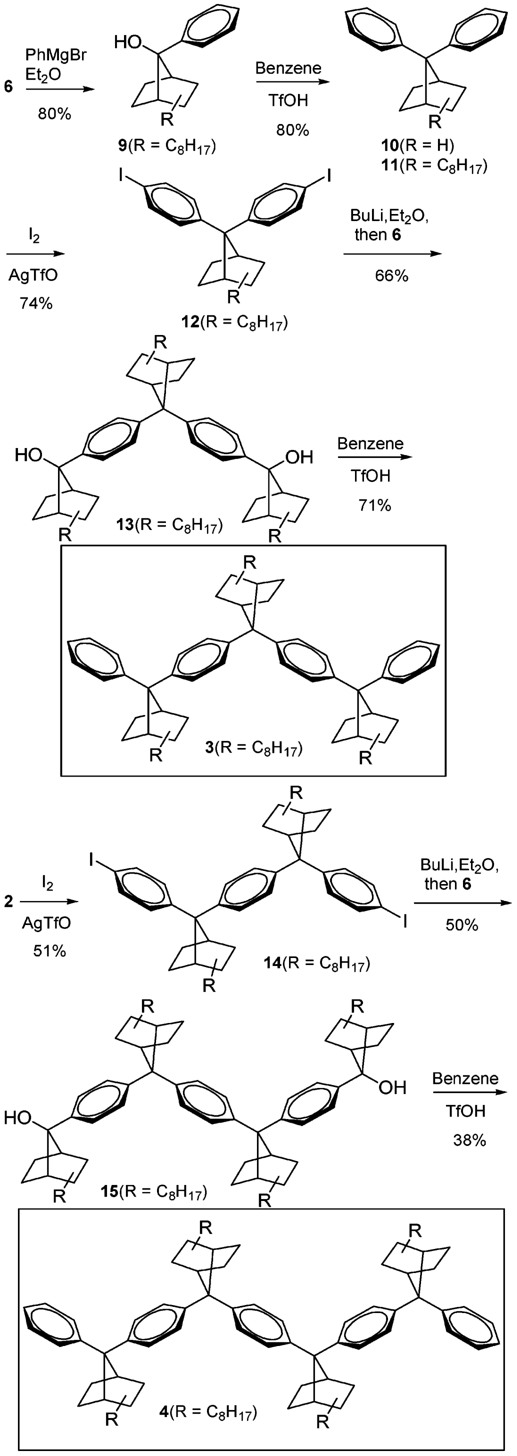


1 and 2. Alkyl chains (*endo*-2-C_8H_{17}) in the cases of **2**, **3**, and **4** are introduced in the structure of norbornane in order to increase the solubility of the oligomers since an unsubstituted trimer is quite insoluble.

The methodology described in Schemes 1 and 2 allows the preparation of monodisperse homoconjugated oligomers by simply reacting the corresponding dilithium compounds (prepared from 1,4-diiodobenzene or the diiodides **12** or **14**) with 7-norbornanones **5** or **6**, followed by reaction of the resulting diols **7**, **8**, **13**, or **15** with benzene/TfOH. Addition reactions of aryllithiums to ketone **6** are in agreement with the facial selectivity described for the reaction of alkyl-substituted 7-norbornanones with nucleophiles, and alcohols derived from the *anti* attack are formed as major products.[9] Oligomers with the desired length can be obtained in good yields using this synthetic route. The length of the oligomers can be easily obtained by ^1H NMR from the relation between aromatic and bridgehead protons.

In solution, two stable conformers of dimers **1** and **2** (U-shaped and Z-shaped) are in equilibrium, both with almost the same energy (isoenergetics), according to semiempirical calculations (PM3 and AM1) (Figure 1). This situation can be extrapolated to trimer **3** and tetramer **4** considering that the number of stable conformations increases with chain length. Therefore, unlike oligobenzyls,[10] in which the rotation of the C−aryl bond is not restricted, DPN oligomers can be considered as open chain but preorganized structures. As a consequence, these oligomers could be used as receptor molecules (molecular clips or tweezers) capable of binding metal cations, such as Ag^+,[11] or neutral electron-deficient molecules[12] since the **1-U** conformer (or the analogous closed conformers in the cases of **3** and **4**) affords an electron-rich environment to the coordination of the guests.

Scheme 2. Synthesis of DFN Trimer **3** and Tetramer **4**



In the solid state, X-ray diffraction analysis (Figure 2) shows that **1** crystallizes, adopting the Z-shaped (zigzag) conformation. This crystal packing is stabilized by CH−π

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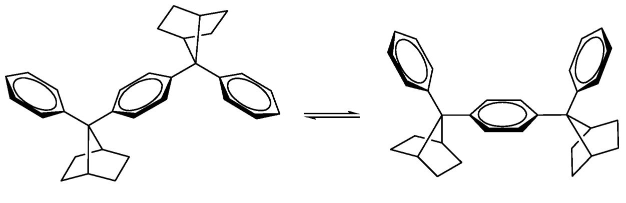
1-Z 1-U

Figure 1. Z- and U-shaped conformers of dimer **1**.

interactions between the *para* hydrogen atom of one molecule and the central aryl ring of the neighboring dimer,[13] a disposition that resembles the T-shaped edge-to-face aromatic interaction in the benzene dimer.[14] Both aryl rings in **1** are almost perpendicular (93.9°), and the distance between the centroids of the arenes is 5.14 Å. The CH$-\pi$ distance is 2.69 Å, well below the sum of the corresponding van der Waals radii (1.2 Å for C$-$H plus 1.7 Å for a half-thickness of the aryl ring). All these values are typical of CH$-\pi$ interaction.[13] However, no $\pi-\pi$ interactions are observed between two adjacent parallel aromatic rings since the inter-ring distance (3.63 Å) is clearly larger than the sum of the van der Waals radii of aryl rings (3.40 Å).[15]

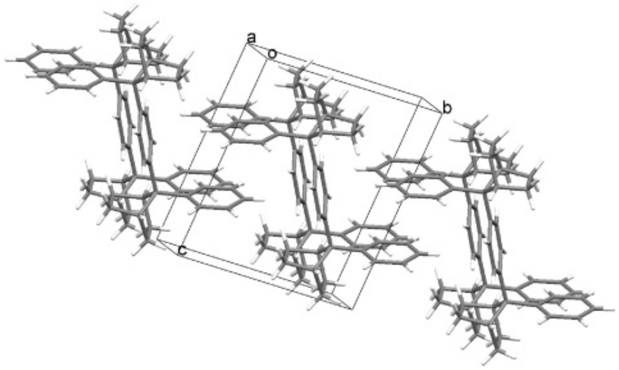

Figure 2. Crystal packing of dimer **1**.

We have previously described that the electronic spectra of DPN and its derivatives show an additional band which is not observed in diphenylmethanes (Figure 3, Table 1). The origin of this band is the preferred cofacial disposition of the aryl rings. Therefore, this absorption is a consequence of the homoconjugation between the aromatic systems.[8,16] Consequently, electronic delocalization by means of aromatic homoconjugation in DPNs can be evaluated by UV spectroscopy.[7]

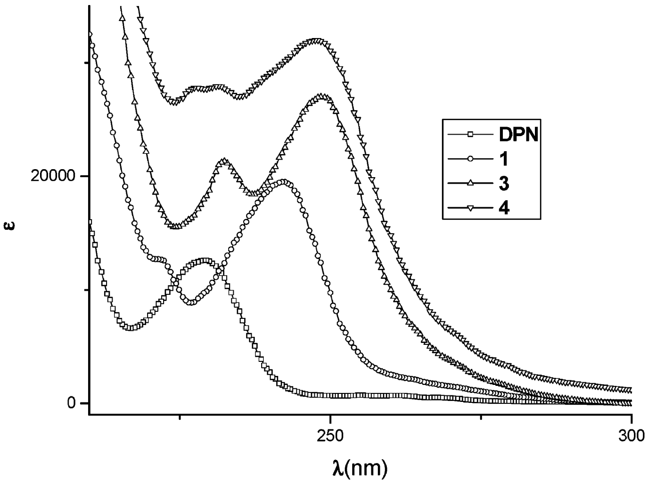

Figure 3. Electronic spectra in hexane of DPN, **1**, **3**, and **4**.

Table 1. Electronic Spectra Data in Hexane of DPN, **1**, **3**, and **4**

	$\lambda_{\max}$	ϵ 10^{-3}	ϵ $10^{-3}/n$
DPN	228	12.6	12.6[a] (6.3)[b]
1	242	19.5	9.75[a] (6.5)[b]
	(222)	(11.0)	
3	248	27.0	9.0[a] (6.7)[b]
	(232)	(21.0)	
4	250	32.0	8.0[a] (6.4)[b]
	(231)	(28.0)	
	(228)	(27.8)	

[a] Considering n = number of DPN subunits. [b] Considering n = number of aryl rings.

Figure 3 shows the electronic spectra of dimer **1**, trimer **3**, and tetramer **4** as well as DPN. As can be seen, the characteristic homoconjugation band of DPN, centered at 228 nm (ϵ = 12 600), is bathochromically and hyperchromically shifted as the chain length of the oligomers increases. Extension of chromophore homoconjugation shifts the longest wavelength absorption maximum ($\lambda_{\max}$) at 242 nm (ϵ = 19 500) in **1** ($\Delta\lambda$ = 14 nm), at 248 nm (ϵ = 27 000) in **3** ($\Delta\lambda$ = 6 nm), and 250 nm (ϵ = 32 000) in **4** ($\Delta\lambda$ = 2 nm) (Table 1).

From the absorption increments of the homoconjugation bands of the oligomers **1**−**4**, it can be concluded that saturation of the bathochromic shift is reached for oligomers n = 4 and 5 since, on going from the trimer **3** to the tetramer

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4, an increase of only 2 nm is observed. The ϵ values also increase with chain length of the oligomers, but ϵ/n remains in the range of $(9.0 \pm 1.0) \times 10^3$ (considering n as number of DPN subunits) or $(6.5 \pm 0.2) \times 10^3$ (considering n as number of aryl rings). Therefore, the limiting value of the wavelength in this type of system can be estimated to be in the range of 4−5 monomeric units (tetramer or pentamer).

In conjugated oligomers and polymers, the number of repeat units required to furnish size-independent properties (redox, optical, electronic) defines the effective conjugation length (ECL) of the molecular wire.[17] By analogy with conjugated oligomers, the effective homoconjugation length (EHL) for homoconjugated oligomers can be also defined for the first time. Therefore, for the homoconjugated molecular wires described in this work, the EHL can be estimated to be in the range of 4−5 DPN subunits. This is important information in order to achieve further studies on photoinduced electron- and energy-transfer processes or NLO[16] properties employing homoconjugated wires.

In summary, an efficient and convenient synthetic methodology for the preparation of new monodisperse homoconjugated molecular wires, derived from cofacial DPN, has been developed. The effective homoconjugation length (EHL) in these oligomers has been estimated to be in the range of 4−5 DPN subunits (5−6 homoconjugated cofacial aryl rings). We are currently investigating the applications of these wires in photoinduced electron- and energy-transfer processes and compounds with NLO properties, as well as its use as open chain preorganized ligands able to form stable complexes with cations and neutral guests.

Acknowledgment. Thanks are due to the Ministerio de Educación y Ciencia of Spain (Research Project CTQ2004-07244-C02-01) for the support of this investigation.

Supporting Information Available: Detailed experimental procedures, full spectroscopic data and crystallographic data of dimer **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

OL071161B

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