

# Donor-substituted peralkynylated “radiaannulenes”: novel all-carbon macrocycles with an intense intramolecular charge-transfer†

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A novel class of planar, highly conjugated all-carbon macrocycles, which we christened “radiaannulenes”, have been prepared based on acetylenic scaffolding using tetraethynylethene (TEE) building blocks; these structures are powerful electron acceptors and, upon peripheral substitution with electron-donating *N,N*-dialkylanilino groups, display intense intramolecular charge-transfer.

Recently, we reported perethynylated expanded radialenes<sup>1</sup> and perethynylated dehydroannulenes<sup>2</sup> bearing peripheral electron-donating *N,N*-dialkylanilino groups and showed that these compounds exhibit strong intramolecular charge-transfer absorptions. Here we present a novel class of mono- (**1–3**) and bicyclic (**4, 5**) expanded acetylenic chromophores which, from a structural viewpoint, are hybrids between perethynylated dehydroannulenes and expanded radialenes and which we therefore call perethynylated radiaannulenes.

The synthesis of **1–3** proceeded via the acyclic precursors **6–8** by intramolecular oxidative acetylene coupling (Scheme 1).<sup>‡</sup> Compounds **6–8** in turn were assembled from the appropriate known mono- and *cis*-bis-deprotected tetraethynylethenes (TEEs),<sup>1–5</sup> also by acetylene coupling (ESI).

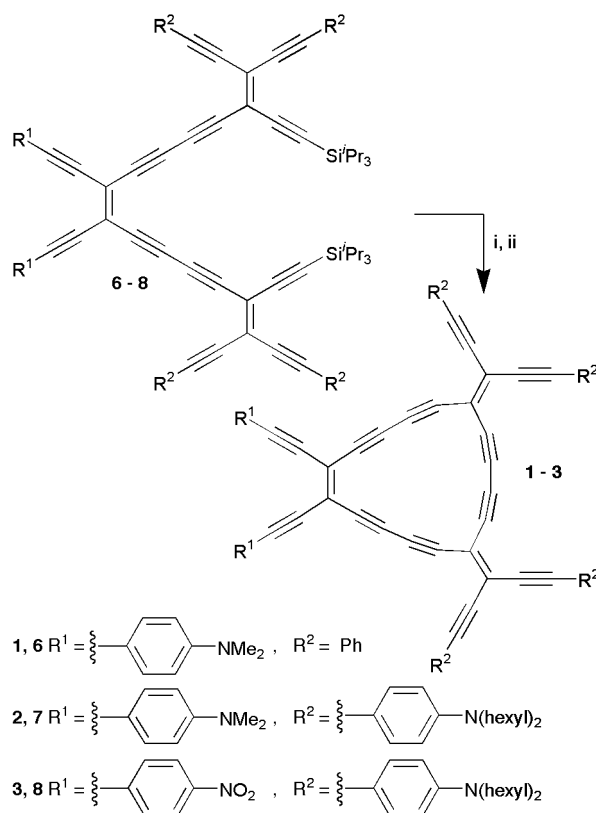
Single crystals of **1**, suitable for X-ray crystallography, were grown by slow diffusion of hexane into a chloroform solution.<sup>§</sup> The cyclic framework is virtually planar, with a mean out-of-plane deviation of 0.040 Å and a maximum deviation of 0.091 Å (C(6)) (Fig. 1). The bond angles around the C(1)–C(16) double bond are all close to the ideal angle of 120° (117.0–122.0°). Strain in the 16-membered ring is expressed mainly at the macrocyclic C=C(sp<sup>2</sup>) angles (C(4)–C(5)–C(6), C(6)–C(7)–C(8), C(9)–C(10)–C(11) and C(11)–C(12)–C(13)) with a bending from ideally 180° to approximately 163°.

The synthesis of the bicyclic scaffolds **4** and **5** was achieved by double intramolecular oxidative coupling of the novel acyclic TEE-pentamers **9** and **10** (Scheme 2), after removal of the silyl-protecting groups. The acetylenic pentamers in turn were obtained from fully deprotected TEE (C<sub>10</sub>H<sub>4</sub>) and appropriate mono-deprotected TEEs by acetylenic coupling (ESI).

The new macrocyclic compounds presented here show several reversible, exceedingly low reduction potentials in cyclic voltammetry experiments (CH<sub>2</sub>Cl<sub>2</sub> + 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>; potentials vs. Fc/Fc<sup>+</sup>), which demonstrates their strong electron-accepting power (ESI). For instance, the first reduction potential of **1** occurs at –1.19 V, compared to –1.96 V for tetrakis(trimethylsilyl)-protected tetraethynylethene.<sup>6</sup> The introduction of four more electron-donating anilino-groups in **2** results in a more negative first reduction potential (–1.34 V) which is virtually identical to that of the recently reported, structurally related hexakis(*N,N*-dimethylanilino)-substituted

peralkynylated dehydro[18]annulene (**11**, see ESI) (–1.36 V in THF).<sup>2</sup> The replacement of two anilino groups in **2** by nitrophenyl groups (**3**) shifts the first reduction potential anodically to –1.07 V. The bicyclic cores **4** and **5** display extremely low first reduction potentials at –0.81 and –0.98 V, respectively. In fact, the potential of **4** is significantly lower than the first reduction potential of buckminsterfullerene C<sub>60</sub> (–1.02 V under comparable conditions),<sup>7</sup> which is touted as a very good electron acceptor.

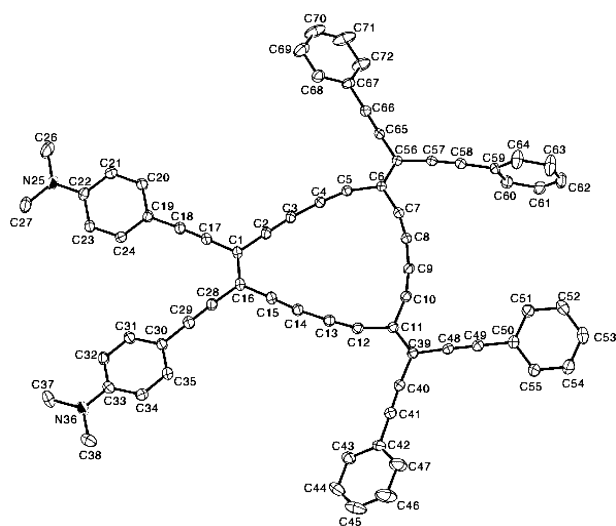
The electron-accepting power of the acetylenic cores in combination with the peripheral electron donor groups gives rise to intense intramolecular charge-transfer (CT) absorptions. The longest-wavelength absorption maximum of the hexa-anilino-substituted monocycle **2** appears at λ<sub>max</sub> = 615 nm (2.02 eV, ε = 99800 M<sup>–1</sup> cm<sup>–1</sup>) (Fig. 2). Upon acidification of the solution with *p*-toluenesulfonic acid (PTSA) and protonation of the donor moieties, this band disappears; neutralisation with triethylamine regenerates the original spectrum (ESI), which proves the CT-character of this absorption. Radiaannulene **1** also undergoes intramolecular CT, but the CT-band is



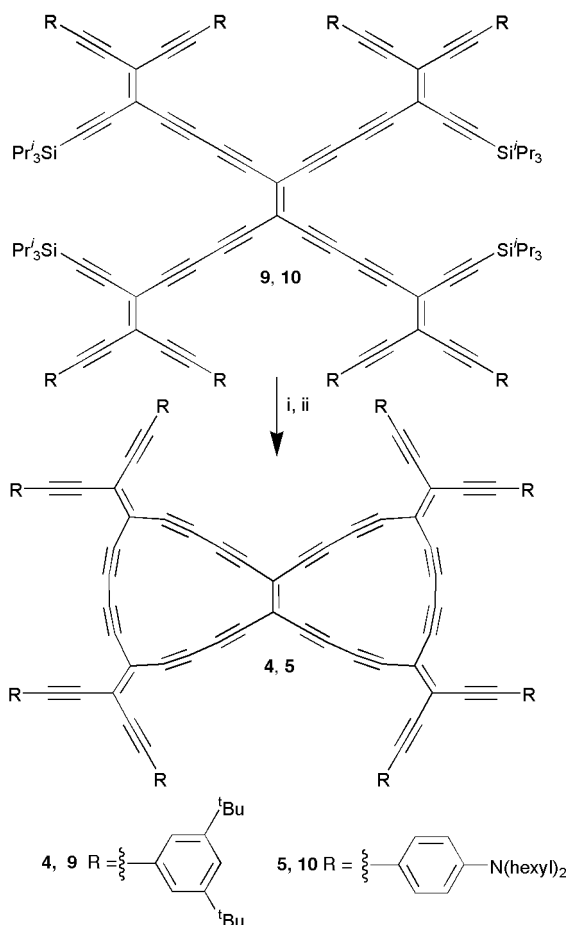
**Scheme 1** Synthesis of monocycles **1–3**. Reagents and conditions: i, Bu<sub>4</sub>NF, THF, 0 °C, 10 min; ii, CuCl, *N,N,N',N'*-tetramethylethylenediamine (TMEDA), O<sub>2</sub>, acetone, r.t., 2 h, 48% (**1**), 32% (**2**), 14% (**3**).

† Electronic supplementary information (ESI) available: schemes describing the full synthesis of **1–5**, preparation and full spectral characterisation of **4**, complete electronic absorption spectra, complete electrochemical data. See <http://www.rsc.org/suppdata/cc/b3/b304130a/>

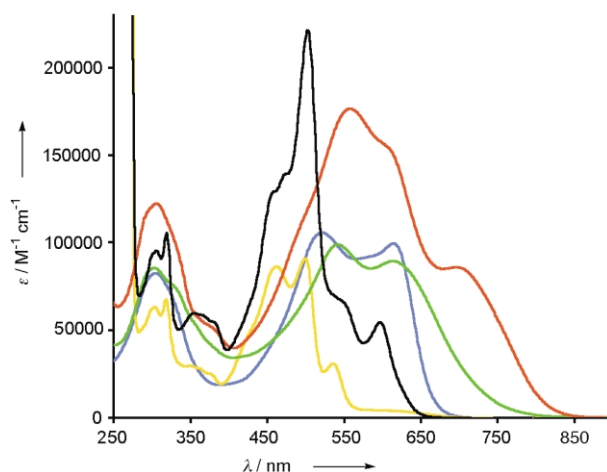
weaker and only observed as a shoulder at 588 nm (2.11 eV) as a result of the smaller number of electron donor moieties. The introduction of two *p*-nitrophenyl moieties into **3** shifts the end-absorption bathochromically by approximately 100 nm (0.22 eV) compared to that of **2**.



**Fig. 1** ORTEP plot of **1** with arbitrary numbering. H-atoms are omitted for clarity. Atomic displacement parameters at 183 K are drawn at the 30% probability level. Selected bond angles ( $^{\circ}$ ): C(4)–C(5)–C(6) 163.18(18), C(5)–C(6)–C(7) 111.76(14), C(6)–C(7)–C(8) 164.86(18), C(9)–C(10)–C(11) 163.88(19), C(10)–C(11)–C(12) 111.18(15), C(11)–C(12)–C(13) 162.78(17).



**Scheme 2** Synthesis of bicycles **4** and **5**. *Reagents and conditions*: i,  $\text{Bu}_4\text{NF}$ , THF,  $0^{\circ}\text{C}$ , 10 min; ii,  $\text{CuCl}$ , TMEDA,  $\text{O}_2$ , acetone/PhH, THF, r.t., 2 h, 88% (**4**), 15% (**5**).



**Fig. 2** Electronic absorption spectra of **2** (blue), **3** (green) and **5** (red) in pure  $\text{CHCl}_3$  and after addition of PTSA (**2**: yellow, **5**: black).

The bicyclic radiannulene **5** displays an unusually strong CT-absorption with an end-absorption at approximately 850 nm (1.46 eV), the lowest-energy end-absorption known for any TEE-oligomers. Again, the CT-band of **5** can be reversibly removed and regenerated by acidification/neutralisation (Fig. S2, ESI $^{\dagger}$ ).

In summary, two-dimensional acetylenic scaffolding based on TEE-building blocks has been advanced to the preparation of radiannulenes, an unprecedented class of perethynylated all-carbon macrocycles that are hybrids between expanded radiolenes and dehydroannulenes. The new carbon sheets are powerful electron acceptors and, upon peripheral donor-substitution, exhibit strong intramolecular charge-transfer absorptions.

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## Notes and references

$\ddagger$  All new compounds were fully characterised by IR, UV/Vis,  $^1\text{H}$  and  $^{13}\text{C}$  NMR, mass spectrometry and microanalysis or HR-MS. All mono- and bicyclic radiannulenes are stable at room temperature in the air for months.

$\S$  *Crystal data* for **1** at 183 K for ( $\text{C}_{70}\text{H}_{40}\text{N}_2$ ,  $M_r = 909.04$ ): triclinic, space group  $P\bar{1}$  (no. 2),  $D_c = 1.167 \text{ g cm}^{-3}$ ,  $Z = 2$ ,  $a = 13.6643(5)$ ,  $b = 14.0449(6)$ ,  $c = 15.9105(8) \text{ \AA}$ ,  $\alpha = 66.12(1)$ ,  $\beta = 68.03(1)$ ,  $\gamma = 83.06(1)^{\circ}$ ,  $V = 2587.6(2) \text{ \AA}^3$ . Bruker-Nonius Kappa-CCD diffractometer, Mo- $\text{K}\alpha$  radiation,  $\lambda = 0.7107 \text{ \AA}$ . A black single crystal with linear dimensions of ca.  $0.3 \times 0.07 \times 0.05 \text{ mm}$  was obtained by slow diffusion of hexane into a  $\text{CHCl}_3$  solution. Final  $R(F) = 0.060$ ,  $wR(F^2) = 0.129$  for 690 parameters and 7437 reflections with  $I > 2\sigma(I)$  and  $2.65 < \theta < 27.49^{\circ}$  (corresponding  $R$ -values based on all 11698 reflections are 0.108 and 0.151 respectively). CCDC reference number 208124. See <http://www.rsc.org/suppdata/cc/b3/b304130a/> for crystallographic data in CIF or other electronic format.

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