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 radialenes¹ and perethynylated dehydroannulenes² bearing peripheral electrondonating *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).‡ Compounds **6–8** in turn were assembled from the appropriate known mono- and *cis*-bis-deprotected tetraethynylethenes (TEEs),^{1–5} 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.§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–C(sp²) 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 ($C_{10}H_4$) 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 (CH₂Cl₂ + 0.1 M Bu₄NPF₆; potentials *vs.* Fc/Fc⁺), 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.⁶ 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

† 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/

peralkynylated dehydro[18]annulene (**11**, see ESI[†]) (-1.36 V in THF).² 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 C₆₀ (-1.02 V under comparable conditions),⁷ 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 $\lambda_{max} = 615$ nm (2.02 eV, $\varepsilon = 99800 \text{ M}^{-1} \text{ cm}^{-1}$) (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_4NF , THF, 0 °C, 10 min; ii, CuCl, *N*,*N*',*N*'-tetramethylethylenediamine (TMEDA), O₂, acetone, r.t., 2 h, 48% (1), 32% (2), 14% (3).

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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 (°): 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, Bu_4NF , THF, 0 °C, 10 min; ii, CuCl, TMEDA, O₂, 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 CHCl₃ and after addition of PTSA (**2**: yellow, **5**: black).

The bicyclic radiaannulene **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 radiaannulenes, an unprecedented class of perethynylated allcarbon macrocycles that are hybrids between expanded radialenes and dehydroannulenes. The new carbon sheets are powerful electron acceptors and, upon peripheral donorsubstitution, exhibit strong intramolecular charge-transfer absorptions.

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Notes and references

[‡] All new compounds were fully characterised by IR, UV/Vis, ¹H and ¹³C NMR, mass spectrometry and microanalysis or HR-MS. All mono- and bicyclic radiaannulenes are stable at room temperature in the air for months.

§ *Crystal data* for **1** at 183 K for (C₇₀H₄₀N₂, *M*_r = 909.04): triclinic, space group *P*Ī (no. 2), *D*_c = 1.167 g cm⁻³, *Z* = 2, *a* = 13.6643(5), *b* = 14.0449(6), *c* = 15.9105(8) Å, *α* = 66.12(1), *β* = 68.03(1), *γ* = 83.06(1)°, *V* = 2587.6(2) Å³. Bruker-Nonius Kappa-CCD diffractometer, Mo-Kα radiation, *λ* = 0.7107 Å. A black single crystal with linear dimensions of *ca*. 0.3 × 0.07 × 0.05 mm was obtained by slow diffusion of hexane into a CHCl₃ solution. Final *R*(*F*) = 0.060, *wR*(*F*²) = 0.129 for 690 parameters and 7437 reflections with *I* > 2*σ*(*I*) and 2.65 < *θ* < 27.49° (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.

- M. B. Nielsen, M. Schreiber, Y. G. Baek, P. Seiler, S. Lecomte, C. Boudon, R. R. Tykwinski, J.-P. Gisselbrecht, V. Gramlich, P. J. Skinner, C. Bosshard, P. Günter, M. Gross and F. Diederich, *Chem. Eur. J.*, 2001, 7, 3263.
- 2 F. Mitzel, C. Boudon, J.-P. Gisselbrecht, M. Gross and F. Diederich, *Chem. Commun.*, 2002, 2318.
- 3 For a review on carbon-rich acetylenic scaffolding, see: F. Diederich, *Chem. Commun.*, 2001, 219.
- 4 J. Anthony, A. M. Boldi, Y. Rubin, M. Hobi, V. Gramlich, C. B. Knobler, P. Seiler and F. Diederich, *Helv. Chim. Acta*, 1995, **78**, 13.
- 5 R. R. Tykwinski, M. Schreiber, R. P. Carlón, F. Diederich and V. Gramlich, *Helv. Chim. Acta*, 1996, **79**, 2249.
- 6 C. Boudon, J.-P. Gisselbrecht, M. Gross, J. Anthony, A. M. Boldi, R. Faust, T. Lange, D. Philp, J.-D. van Loon and F. Diederich, J. Electroanal. Chem., 1995, **394**, 187.
- 7 (a) D. Dubois, G. Moninot, W. Kutner, M. T. Jones and K. M. Kadish, J. Phys. Chem., 1992, 96, 7137; (b) L. Echegoyen, F. Diederich and L. Echegoyen, in Fullerenes: Chemistry, Physics and Technology, eds. K. D. Kadish and R. S. Ruoff, Wiley-VCH, New York, 2000, p. 1.