

π -Electron conjugation effects in antiaromatic dehydro[12]- and aromatic dehydro[18]-annulenes

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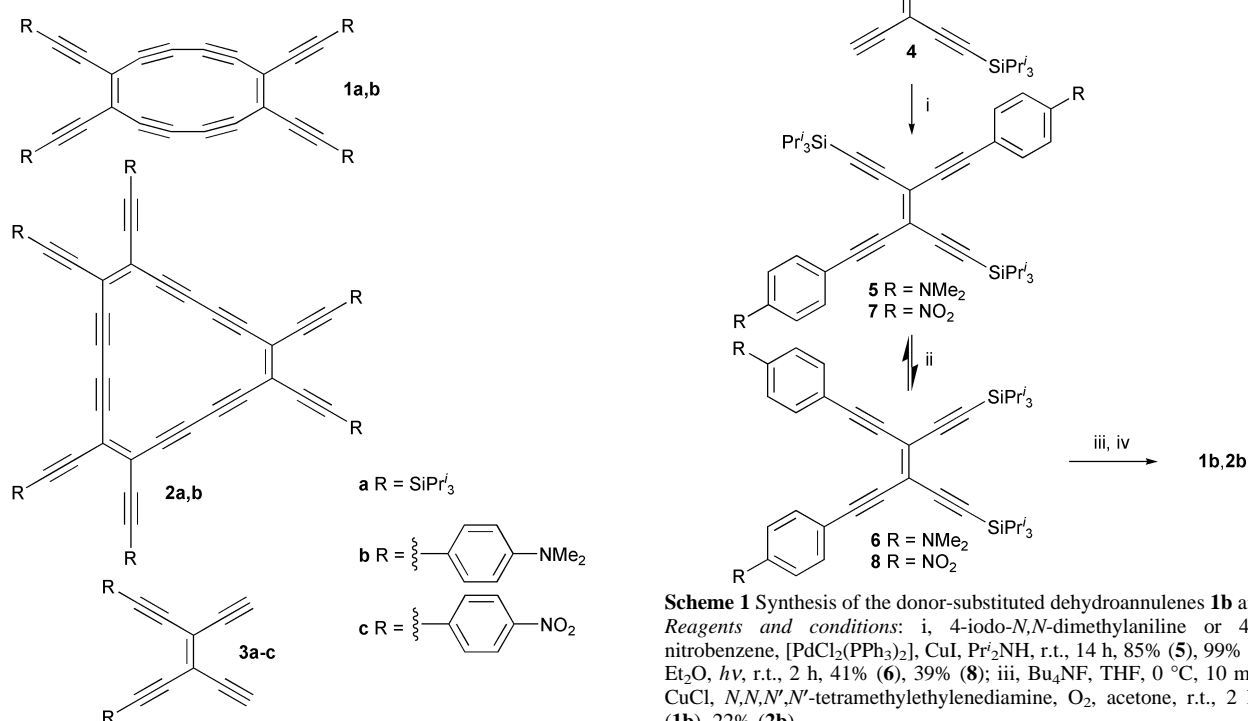
N,N-Dimethylanilino-substituted perethynylated dehydro[12]- and dehydro[18]-annulenes were prepared by oxidative acetylenic coupling of *cis*-bisdeprotected tetraethynylethene derivatives obtained by a new photochemical route; they display strongly bathochromically shifted longest-wavelength absorption bands compared to their silyl-substituted counterparts resulting from efficient intramolecular charge-transfer between the peripheral π -electron donors and the electron-accepting central acetylenic core.

Although aromatic and antiaromatic dehydroannulenes have been the subject of numerous investigations,^{1,2} little is known about the propagation of π -electron donor–acceptor conjugation across these macrocyclic perimeters. We had earlier reported the preparation of the per(silylethynylated) dehydroannulenes **1a** and **2a** by oxidative coupling of *cis*-bisdeprotected tetraethynylethene (TEE) **3a** and shown spectroscopically that the smaller [12]annulene perimeter is paratropic whereas the larger [18]annulene is diatropic.³ With their many conjugated C(sp)-atoms, the all-carbon cores of these annulenes are strong electron acceptors as revealed by electrochemical investigations, with the reduction of antiaromatic **1a** expectedly being facilitated when compared with **2a**.^{4,5} We have for some time been inspired to functionalise these planar perimeters with donor/acceptor groups in order to investigate intramolecular charge-transfer effects in annulenes. However, *cis*-bisdeprotected TEEs, required for the oxidative macrocyclisation, had only been available by a tedious multistep synthesis including

several highly unstable intermediates,³ which has hitherto prevented the preparation of functionalised derivatives of **1a** and **2a**. Here we disclose a novel, much simpler photochemical route to the donor/acceptor substituted TEEs **3b,c** which now has enabled the preparation and subsequent spectroscopic investigation of the perethynylated dehydroannulenes **1b** and **2b** bearing lateral *N,N*-dimethylanilino substituents.

Pd-catalysed Sonogashira cross-coupling of *trans*-bisdeprotected TEE **4**, which is readily available by a short synthetic route,⁶ with 4-iodo-*N,N*-dimethylaniline afforded the *trans*-bis-donor-substituted TEE **5** in 85% yield (Scheme 1).⁷ Irradiation of **5** in diethyl ether with a medium-pressure Hg-lamp (125 W) for 2 h led to photochemical equilibration between the *cis*- and the *trans*-isomers.⁸ The diastereoisomeric mixture was separated by column chromatography (SiO₂, hexane/CH₂Cl₂ 1:1), yielding 41% of the desired *cis*-TEE **6** along with 53% of the *trans*-isomer **5** that can be recycled. The same procedure was applied to generate *trans*-**7** and subsequently the *cis*-bis(nitrophenyl)-substituted TEE **8**.[†]

Silyl-deprotection of **6** was accomplished with Bu₄NF in moist THF. The *cis*-bisdeprotected TEE deteriorates rapidly in neat form but is rather stable in solution. Subjecting the deprotected species to Hay coupling conditions led to the formation of dehydro[12]annulene **1b** and dehydro[18]annulene **2b**, both as deep-purple solids. Higher macrocyclic



Scheme 1 Synthesis of the donor-substituted dehydroannulenes **1b** and **2b**. Reagents and conditions: i, 4-iodo-*N,N*-dimethylaniline or 4-iodo-nitrobenzene, [PdCl₂(PPh₃)₂], CuI, Pr₃NH, r.t., 14 h, 85% (**5**), 99% (**7**); ii, Et₂O, *hν*, r.t., 2 h, 41% (**6**), 39% (**8**); iii, Bu₄NF, THF, 0 °C, 10 min; iv, CuCl, *N,N,N',N'*-tetramethylethylenediamine, O₂, acetone, r.t., 2 h, 2% (**1b**), 22% (**2b**).

oligomers were not detectable in the MALDI-TOF mass spectrum (matrix: 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB)) of the crude reaction mixture. The two macrocycles can be separated by repetitive flash chromatography (SiO₂; hexane/CH₂Cl₂ (1 : 1) → CH₂Cl₂). The ratio of the two formed annulenes is concentration-dependent, however, the isolated yield of the [12]annulene **1b** always remained low as a result of its marked instability, which led to a significant loss of product during work-up and purification. In contrast, the [18]annulene **2b** is remarkably stable and can be handled without problems.† Attempts to apply the same protocol to the preparation of nitrophenyl-substituted dehydroannulenes starting from the corresponding TEE-precursor **8** were not successful.

The UV/Vis spectrum (CHCl₃) of [18]annulene **2b** (Fig. 1) is dominated by a strong, broad longest-wavelength absorption band at $\lambda_{\text{max}} = 518 \text{ nm}$ (2.39 eV; $\epsilon = 105200 \text{ M}^{-1} \text{ cm}^{-1}$) and features an end-absorption (around 700 nm; 1.77 eV) that is bathochromically shifted by more than 200 nm compared to that of the corresponding silyl-substituted derivative **2a** (480 nm, 2.57 eV).³ Upon acidification with toluene-4-sulfonic acid, the colour of the solution changes from purple to yellow, which is the colour of the silyl-substituted derivative **2a**. Accordingly, the intense absorption at 518 nm disappears nearly completely and the absorption spectrum becomes strikingly similar to that of **2a** with the most intense band now being shifted to 427 nm (2.90 eV; **2a**: 405 nm, 3.06 eV). The residual absorptivity above 500 nm in the acidified solution may be explained by incomplete hexa-protonation. Neutralisation with triethylamine regenerates the original spectrum of **2b**. This behavior identifies the strong longest-wavelength absorption band at $\lambda_{\text{max}} = 518 \text{ nm}$ as a charge-transfer band, resulting from efficient intramolecular charge-transfer interactions between the electron-donating peripheral anilino groups and the electron-accepting all-carbon core.

In agreement with its antiaromaticity, the silylated [12]annulene **1a** featured a much lower HOMO–LUMO gap (end-absorption near 660 nm, 1.87 eV) than the corresponding aromatic [18]annulene **2a** (480 nm, 2.57 eV), with weak bands between 490 and 620 nm ($\epsilon = 200\text{--}400 \text{ M}^{-1} \text{ cm}^{-1}$) being responsible for its buckminsterfullerene-type magenta–purple colour.³ In the donor-substituted [12]annulene **1b**, these weak bands are now completely overlapped by an intramolecular charge-transfer transition, featuring an absorption maximum at ($\lambda_{\text{max}} = 518 \text{ nm}$ (2.39 eV; $\epsilon = 35100 \text{ M}^{-1} \text{ cm}^{-1}$) and end-absorption (near 700 nm). Like in the case of **2b**, the strong lowest-energy band disappears nearly completely upon acidification (Fig. 1). Thus, both, the [12]annulene **1b** and the

[18]annulene **2b** are capable of mediating π -electron donor–acceptor conjugation. However, the intensity of the charge-transfer band of **1b** is significantly weaker than that of **2b** even when the smaller number of donor–acceptor conjugation paths is taken into account. This is somewhat surprising since one might expect the charge-transfer to be more efficient in the [12]annulene as the uptake of electrons reduces the antiaromaticity whereas in the case of the [18]annulene, the uptake of electrons is accompanied by a loss of aromaticity. Clearly, the nature of the electronic transitions in these compounds is governed by additional factors that have yet to be elucidated in theoretical calculations.

The redox properties of the dehydro[18]annulene **2b** were examined by cyclic voltammetry (CV) on a glassy carbon working electrode in THF solution with 0.1 M Bu₄NPF₆ as the supporting electrolyte. The CV features two well-resolved reversible one-electron reduction steps (−1.36 and −1.72 V, vs. the ferrocene/ferricenium couple) demonstrating the electron-acceptor properties of the central C₃₀ core. The two reduction steps occur at more negative potential than those of **2a** (−1.12 and −1.52 V)⁴ which is readily explained with the higher electron density in the all-carbon core inflicted by the six anilino groups. Additionally, the CV shows an irreversible third reduction step at −2.27 V (peak potential at 0.1 V s^{−1}) and a reversible, two-electron oxidation step at +0.25 V that can be attributed to the oxidation of two, out of six, anilino groups. The remaining anilino groups were oxidised in an irreversible unresolved peak whose potential was observed at +0.4 V ($v = 0.1 \text{ V s}^{-1}$). The redox properties of **1b** could not be studied due to its instability.

In summary, a straightforward photochemical access to *cis*-bisdeprotected TEEs has enabled the synthesis of novel *N,N*-dimethylamino-substituted perethynylated dehydro[12]- and dehydro[18]-annulenes. As a result of the acetylenic spacers between the donor groups and the electron-accepting macrocyclic perimeters, the novel chromophores adopt a fully planar geometry and undergo intense intramolecular charge-transfer interactions.

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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.

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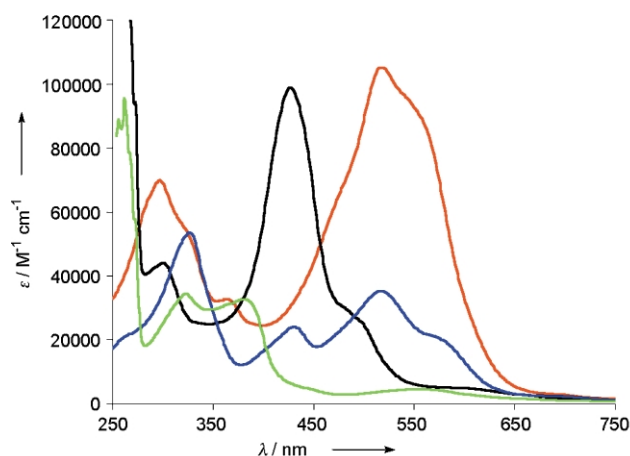


Fig. 1 Electronic absorption spectra of **1b** (blue) and **2b** (red) in pure CHCl₃ and after addition of toluene-4-sulfonic acid (green, **1b** and black, **2b**).