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

Frieder Mitzel,[a] Corinne Boudon,[b] Jean-Paul Gisselbrecht,[b] Maurice Gross[b] and François Diederich*[a]

[a] *Laboratorium für Organische Chemie, ETH-Hönggerberg, CH-8093, Zürich, Switzerland.*
E-mail: diederich@org.chem.ethz.ch
[b] *Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide, UMR 7512, C.N.R.S, Université Louis Pasteur, 4, rue Blaise Pascal, 67000, Strasbourg, France*

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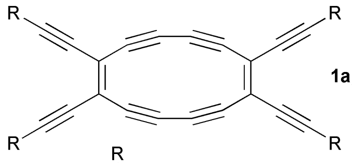
***N*,*N*-Dimethylanilino-substituted perethynylated dehydro[12]- and dehydro[18]-annulenes were prepared by oxidative acetylenic coupling of *cis*-bisdeprotected tetraethynylethene derivatives obtained by a new photochemical route; they display strongly bathochromically shifted longest-wavelength absorption 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.**

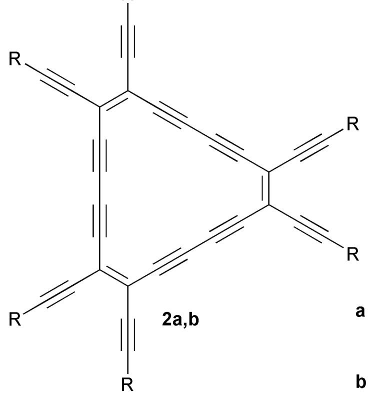
Although aromatic and antiaromatic dehydroannulenes have been the subject of numerous investigations,[1,2] little is known about the propagation of π-electron donor–acceptor conjugation across these macrocyclic perimeters. We had earlier reported the preparation of the per(silylethynylated) dehydroannulenes **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 (SiO$_2$, hexane/CH$_2$Cl$_2$ 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**.†

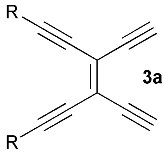
Silyl-deprotection of **6** was accomplished with Bu$_4$NF in moist THF. The *cis*-bisdeprotected TEE deteriorates rapidly in neat form but is rather stable in solution. Subjecting the deprotected species to Hay coupling conditions led to the formation of dehydro[12]annulene **1b** and dehydro[18]annulene **2b**, both as deep-purple solids. Higher macrocyclic



1a,b

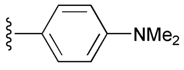


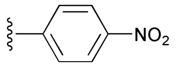
2a,b

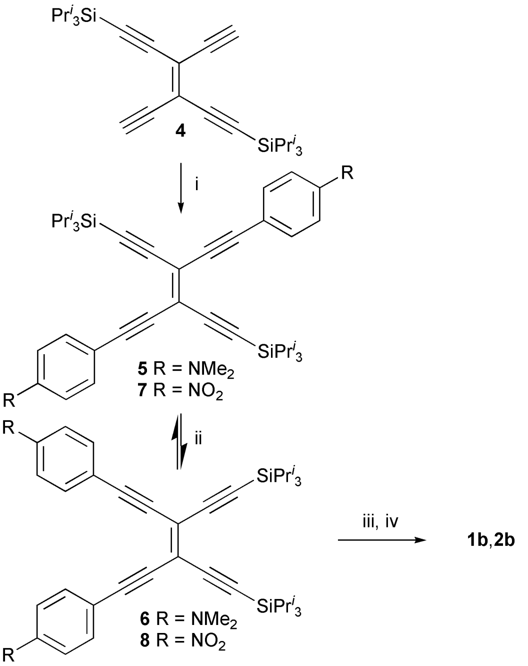


3a-c

a R = SiPr$^i_3$

b R =


c R =




Scheme 1 Synthesis of the donor-substituted dehydroannulenes **1b** and **2b**. *Reagents and conditions*: i, 4-iodo-*N*,*N*-dimethylaniline or 4-iodonitrobenzene, [PdCl$_2$(PPh$_3$)$_2$], CuI, Pr$^i_2$NH, r.t., 14 h, 85% (**5**), 99% (**7**); ii, Et$_2$O, *hν*, r.t., 2 h, 41% (**6**), 39% (**8**); iii, Bu$_4$NF, THF, 0 °C, 10 min; iv, CuCl, *N*,*N*,*N′*,*N′*-tetramethylethylenediamine, O$_2$, acetone, r.t., 2 h, 2% (**1b**), 22% (**2b**).

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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 (SiO_2; hexane/CH_2Cl_2 (1 : 1) → CH_2Cl_2). 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 ($CHCl_3$) of [18]annulene **2b** (Fig. 1) is dominated by a strong, broad longest-wavelength absorption band at λ_{max} = 518 nm (2.39 eV; ε = 105200 M^{-1} 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 λ_{max} = 518 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 (ε = 200–400 M^{-1} 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 (λ_{max} = 518 nm (2.39 eV; ε = 35100 M^{-1} 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.

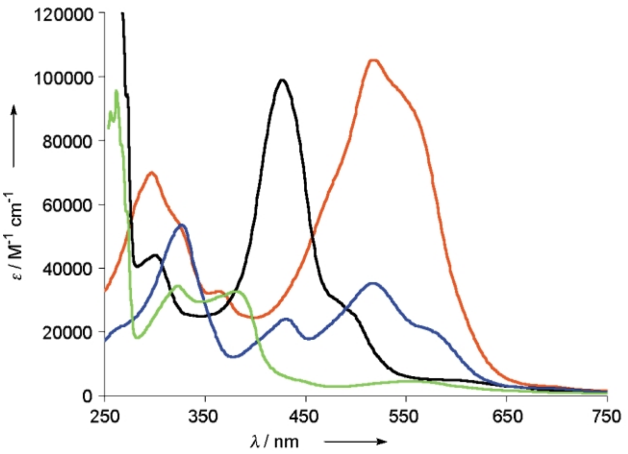

Fig. 1 Electronic absorption spectra of **1b** (blue) and **2b** (red) in pure $CHCl_3$ and after addition of toluene-4-sulfonic acid (green, **1b** and black, **2b**).

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 Bu_4NPF_6 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 C_{30} 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 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 ^{13}C NMR, mass spectrometry and microanalysis.

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