

Spiro Compounds

From Homoconjugated Push–Pull Chromophores to Donor– Acceptor-Substituted Spiro Systems by Thermal Rearrangement

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In memoriam Michael Bendikov

Abstract: Series of homoconjugated push-pull chromophores and donor-acceptor (D-A)-functionalized spiro compounds were synthesized, in which the electron-donating strength of the anilino donor groups was systematically varied. The structural and optoelectronic properties of the compounds were investigated by X-ray analysis, UV/Vis spectroscopy, electrochemistry, and computational analysis. The homoconjugated push-pull chromophores with a central bicyclo[4.2.0]octane scaffold were obtained in high yield by [2+2] cycloaddition of 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) to N,N-dialkylanilino- or N,N-diarylanilino-substituted activated alkynes. The spirocyclic compounds were formed by thermal rearrangement of the homoconjugated adducts. They also can be prepared in a one-pot reaction starting from DDQ and anilino-substituted alkynes. Spiro products with N,N-diphenylanilino and N,N-diisopropylanilino groups were isolated in high yields whereas compounds

Introduction

Planar and non-planar push-pull chromophores (D- π -A) consisting of strong electron donors and acceptors, have been extensively investigated due to their interesting optoelectronic properties resulting from intramolecular charge transfer (CT).^[1] Most of the known push-pull systems are planar to retain effi-

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with pyrrolidino, didodecylamino, and dimethylamino substituents gave poor yields, with formation of insoluble side products. It was shown by in situ trapping experiments with TCNE that cycloreversion is possible during the thermal rearrangement, thereby liberating DDQ. In the low-yielding transformations, DDQ oxidizes the anilino species present, presumably via an intermediate iminium ion pathway. Such a pathway is not available for the N,N-diphenylanilino derivative and, in the case of the N,N-diisopropylanilino derivative, would generate a strained iminium ion (A1,3 strain). The mechanism of the thermal rearrangement was investigated by EPR spectroscopy, which provides good evidence for a proposed biradical pathway starting with the homolytic cleavage of the most strained (CN)C-C(CN) bond between the fused four- and six-membered rings in the homoconjugated adducts.

cient linear D–A π -conjugation.^[2] Organic materials in optoelectronic devices are often used in the form of thin films, and the morphology of the films must be carefully controlled.^[3] Non-planar, linearly conjugated push–pull systems have crucial advantages in this respect as their structural features lead to improved solubility and processability and ensure the desired amorphous character of the resulting films. Therefore, they represent attractive targets for application in advanced functional materials.^[4,5]

Intramolecular CT interactions have also been investigated in chromophores, where appropriately aligned, rigid, non- π conjugating spacers separate the donor and acceptor π -systems. Examples are through-space CT interactions in donor–acceptor cyclophanes^[6,7] and through-bond CT interactions via rigid σ -bond frameworks.^[8] Only a few studies report on homoconjugated CT interactions in chromophores with a non-parallel arrangement of donor and acceptor groups.^[9]

In our ongoing development of non-planar push-pull chromophores available by a click-chemistry-type [2+2] cycloaddition-retroelectrocyclization (CA-RE) cascade between electronrich alkynes and electron-deficient alkenes, we became interested in expanding the variety of the olefinic electron accept-

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Results and Discussion

Syntheses of homoconjugated adducts (\pm)-2 a-h and D-A- π -conjugated spiro compounds (\pm)-3 a-e

Target homoconjugated pushpull chromophores (\pm) -2a-h were prepared from various anilino-substituted alkynes 1a-h by the one-step procedure described earlier.^[13] Thermal [2+2] cycloaddition of DDQ with the alkynes proceeded smoothly in 1,2-dichloroethane at 25°C, and the desired novel DDQ adducts (\pm) -**2a**-**h** were obtained in high isolated yields (76 - 94%)(Table 1). All homoconjugated

ors beyond the commonly used cyanoolefins, such as tetracyanoethene (TCNE) and 7,7,8,8-tetracyano-p-quinodimethane (TCNQ).^[1c,d, 10, 11] Among others,^[12] we explored the use of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ),^[13] a well-known oxidizing reagent for dehydrogenation reactions.^[14] We observed facile [2+2] cycloaddition to electron-rich alkynes under formation of homoconjugated push-pull chromophores featuring a bicyclo[4.2.0]octane scaffold, with interesting optoelectronic properties including high third-order optical nonlinearities.^[13] While the cycloaddition was not followed by the usual retroelectrocyclization, in one example, an unexpected thermal rearrangement to the first member of a new class of π -conjugated D-A-functionalized spiro compounds was observed. Other examples of thermal [2+2] cycloadditions of DDQ with electron-rich alkynes have independently also been reported recently.[15, 16]

conjugated spiro compounds (\pm) -**3** a-e formed by thermal rearrangement.

Starting from a series of differently *N*-substituted anilinoacetylenes **1 a**–**h** (Figure 1), we report here the high-yield preparation and optoelectronic properties of the homoconjugated D– A-substituted bicyclo[4.2.0]octanes (\pm) -**2 a**–**h** formed upon reaction with DDQ. Subsequently, the scope of the thermal rearrangement to the linearly D–A-conjugated spirocyclic systems (\pm) -**3 a**–**e** is investigated as well as the structures and optoelectronic properties of these novel chromophores. The yields of this unusual transformation differ greatly, depending on the *N*-substituents, and we describe a series of experimental studies to provide an interpretation of these findings. The novel rearrangement was also investigated by electron paramagnetic resonance (EPR) studies, and a biradical reaction mechanism is proposed.

Table 1. [2+2] Cycloaddition of alkynes with DDQ.								
R ²	$R^{1} \xrightarrow{\text{DDQ},} R^{2} \xrightarrow{\text{CI}} R^{2}$ $R^{1} \xrightarrow{\text{(CH}_{2}\text{CI})_{2}, 25 \text{ °C},} 0.5 \text{ h} \xrightarrow{\text{CI}} R^{2}$ $R^{1} \xrightarrow{\text{CI}} R^{2}$							
1a-h		(±)-2a-h						
Substrate	R ¹	R ²	Product, Yield [%]					
1a	s ² N	н	(±)- 2 a , 89					
1b	s ^s N ^{Ph} Ph	Н	(±)- 2 b , 81					
1c	ς ^ζ Ν ^{-C₁₂H₂₅ C₁₂H₂₅}	Н	(±)- 2 c , 81					
1 d	^{s^s²} N ∕	н	(±)- 2 d , 76					
1e	s ² N -	Me	(±)- 2 e , 94					
1f	^{رج} _N −C ₃ H7 C ₃ H7	Н	(±)- 2 f , 89					
1g	^ج ري H H	н	(±)- 2 g , 77					
1h	Sr. N	н	(±)- 2 h , 85					

adducts are deeply purple-colored in the solid state and stable at room temperature.

Subsequently, five representative substrates of the DDQ adducts were chosen to investigate the thermal rearrangement leading to the spiro compounds, for which we had reported a single example in our earlier work.^[13] DDQ adducts (\pm) -**2a**– **e** were dissolved in dry toluene and stirred at reflux tempera-

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Table 2. Synthesis of push-pull spiro compounds (±)-3 a-e.								
	toluene, reflux, 5–24 h R ¹		CI CN R ² O CN R ¹					
(±)-2a-e			(±)-3a-e					
Substrate	R ¹	R ²	Product, Yield [%]					
(±)-2a	s ^z .N	н	(±)- 3 a , 82					
(±)-2 b	s ^s N ^{Ph} Ph	н	(±)- 3 b , 71					
(±)-2c	^{δ²} N ^{-C₁₂H₂₅ C₁₂H₂₅}	н	(±)- 3 c , 10					
(±)-2 d	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	н	(±)- 3 d , 5					
(±)-2 e	s ^{2,} N -	Me	(±)- 3 e , 32					



Scheme 1. One-pot synthesis of spiro compounds (\pm) -3 a,b.

ture. Large differences in the isolated yields of donor-substituted spiro compounds (\pm) -**3a**-**e** were reproducibly obtained: only the *N*,*N*-diisopropyl ((\pm) -**3a**, 82%) and the *N*,*N*-diphenyl ((\pm) -**3b**, 71%) derivatives were formed in high yield, whereas all other products were isolated in low yield (5–32%, Table 2). The transformations of substrates (\pm)-**2c**, (\pm)-**2d**, and (\pm)-**2e** afforded substantial amounts of insoluble, black decomposition products, and the origin of these side reactions was further investigated (see below) after full characterization of the desired products.

All spirocyclic products are highly colored solids and are stable for prolonged periods of time at ambient temperature, but decompose slowly in toluene at reflux. We also prepared spiro compounds (\pm) -**3a** and (\pm) -**3b**, starting from alkynes **1a,b**, in a one-pot reaction with DDQ in toluene at reflux (Scheme 1). Yields were slightly lower ((\pm) -**3a**: 52%; (\pm) -**3b**: 48%) compared to the total yields in the two-step protocol (82% and 71%, respectively), mainly due to purification difficulties after the one-pot synthesis.

X-ray crystal structure analysis

Crystals suitable for X-ray analysis were obtained by slow diffusion of hexane into dichloromethane or ethyl acetate solutions of the chromophores at 20 °C. The structures of the homocon-

jugated compounds (\pm) -2a, (\pm) -2d, and (\pm) -2g (Figures 1SI-3SI in the Supporting Information) confirmed the previously observed^[13] regioselective addition of the alkynes to the double bond of DDQ bearing the two CN groups. The structures of the spiro compounds (\pm) -3a, (\pm) -3b, and (\pm) -3e were also solved (Figure 2). Their N-substituted anilino rings are roughly in plane with the adjacent dicyanocyclopentadiene ring. Various intermolecular orthogonal dipolar interactions, such as CN···CN, CO···CO, CO···CN, CN···CO, as well as π - π interactions are observed in the crystal packings of both homoconjugated and spirocyclic systems (see Figures 8SI and 9SI in the Supporting Information). The quinoid character values^[17] (δr between 0.028 and 0.046; in benzene, δr equals 0, whereas fully quinoid rings show values between 0.08-0.1) were obtained from the experimental bond lengths in the X-ray structures (Figure 7SI) and show high guinoid character for the DAA rings in the ground states of both homoconjugated and π conjugated systems (Table 1SI).

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UV/Vis spectroscopy

The homoconjugated D-A chromophores show intermolecular CT bands (λ_{max} values between 462 and 549 nm; 2.68–2.26 eV) of moderate intensity (ε values between 2000 and $3000 \text{ M}^{-1} \text{ cm}^{-1}$, Figure 10SI). While the absorption maxima of the linearly π -conjugated spirocyclic CT compounds are in a comparable energy range (λ_{max} values between 496 and 530 nm, 2.50-2.34 eV), the molar extinction coefficients are higher by nearly up to one magnitude (ε values between 12700 and 22400 M^{-1} cm⁻¹, Figure 3 and Figure 11SI in the Supporting Information). The CT character of the longest-wavelength absorption in both series of chromophores was proven by protonation- (disappearance of the CT band) re-neutralization (full recovery of the CT band) experiments for all compounds except the diphenylanilino derivatives (\pm) -2b and (\pm) -3b (see Figures 14SI-24SI). The basicity of the amino centers in the latter is most probably not sufficient to enable protonation by CF₃COOH (TFA) to a sizeable extent, and the CT band does therefore not disappear. Both homoconjugated and spirocyclic chromophores feature positive solvatochromism (see Figures 12SI and 13SI).[18]

The increase in electron-donor strength among the various *N*-substituted anilines follows the order established by Weringa and Janssen.^[19] With increasing donor strength, the CT bands are bathochromically shifted. This shift is larger in the homoconjugated than in the linearly π -conjugated spirocyclic systems. CT bands in the former series shift in the following sequence: $\lambda_{max} = 462$ (2.68 eV, (\pm)-2g), 519 (2.39 eV, (\pm)-2b), 523 (2.37 eV, (\pm)-2h), 540 (2.30 eV, (\pm)-2c), 543 (2.29 eV, (\pm)-2e), 546 (2.27 eV, (\pm)-2a), and 549 nm (2.26 eV, (\pm)-2d and (\pm)-2f). In the spectra of the spirocyclic systems, the CT bands appear at $\lambda_{max} = 496$ (2.50 eV, (\pm)-3e), 520 (2.38 eV, (\pm)-3b), 524 (2.37 eV, (\pm)-3d), 530 (2.34 eV, (\pm)-3a), and 530 nm (2.29 eV, (\pm)-3c).^[20]



Electrochemistry

Electrochemical measurements were carried out in CH_2CI_2 containing 0.1 \bowtie nBu_4NPF_6 in a classical three-electrode cell by cyclic voltammetry (CV) and rotating-disk voltammetry (RDV). All potentials are given versus Fc⁺/Fc (ferrocenium/ferrocene couple), which was used as an internal reference. They are summarized in Table 2SI and Figure 25SI in the Supporting Information. For some species, due to electrode inhibition, reproducible results could only be observed on freshly polished working electrodes.

All N-substituted homoconjugated chromophores undergo a reversible one-electron oxidation occurring at the anilino moiety, whereas the reduction occurs in two steps on the dichloro-dicyano-substituted cyclohexenedione ring. The first reduction gives either a reversible one-electron transfer for (\pm) -**2b** (-0.75 V, CV), (\pm)-**2e** (-0.78 V), and (\pm)-**2g** (-0.78 V), or corresponds to an electrochemical-chemical reduction step. At low scan rates, the peak current ratio I_{pa}/I_{pc} (peak anodic current/peak cathodic current) was smaller than unity (at v =0.1 V s⁻¹ $I_{pa}/I_{pc} = 0.7$). When the scan rate was increased, the ratio reached unity at scan rates higher than 1 Vs^{-1} . This behavior is typical for an electrochemical-chemical mechanism where the electrochemical step generates the radical anions, which undergo a chemical reaction. This denotes that the generated radical is only stable at high scan rates and is rather reactive. The second reduction (around -1.5 V) is always irreversible at low scan rates and becomes reversible for (\pm) -2a, (\pm) -**2 f**, (\pm) -**2 g**, and (\pm) -**2 h** at scan rates higher than 5 V s⁻¹. EPR results (see below) also show that the radical ions can be selectively generated and that the spin distribution corresponds to the spin residing in the "amino" and the "dichloro-dicyano-substituted cyclohexenedione" part of the molecule for the oxidation and reduction, respectively.

Spiro species (±)-**3 a**–**e** undergo a reversible one-electron oxidation, whereas the reduction occurs as an irreversible twoelectron transfer at around -1.1 V (Table 2SI, Figure 25SI). For these compounds, the generated radical anion is much more reactive than in the homoconjugated series. The estimations of electrochemical gap ($E_{ox}-E_{red}$) are rather approximate due to the irreversible nature of the reduction step, nevertheless the trends are significant and can be compared with the optical gaps determined from λ_{max} or λ_{end} in the UV/Vis spectra (Table 3SI).

Computational study of the electronic transitions

On the optimized molecular structures of (\pm) -**2a**–**h** and (\pm) -**3a**–**e** (except (\pm) -**2c** and (\pm) -**3c**), the vertical optical transitions were calculated by time-dependent density functional theory (TD-DFT) using the software package Gaussian 09 (for further details on the computational methods see the Supporting Information).^[21] In all cases, the computed transition energies are slightly larger than the experimental values (Tables 4 SI–14SI). Differences between computed excitation energies and experimental absorption maxima are in the range of 0.03–0.23 eV [root-mean-square deviation (RMSD)=0.18 eV] for



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(±)-3e

Figure 2. ORTEP representations of spirocyclic (\pm) -3a, (\pm) -3b (one of the

two symmetry independent molecules shown) and (\pm) -3 e with vibrational

ellipsoids shown at the 50% probability level, T=100 K. Arbitrary number-

N12

ing. H-atoms and solvent molecules are omitted for clarity.



Figure 3. UV/Vis absorption spectra of D–A-functionalized spiro compounds (\pm)-3 a–e.

(±)-**2a**–**h** and in the range of 0.33–0.41 eV (RMSD=0.366 eV) for (±)-**3a**–**e**, well within the expected error for anilino-cyano type push–pull chromophores.^[22–25]

The lowest-energy transitions are composed mostly of HOMO-to-LUMO excitations and thus can be best described as intramolecular charge-transfer processes involving the transfer of electron density from the anilino donor to the dichloro-dicyano-substituted cyclohexenedione acceptor moiety in compounds (\pm) -**2a**-**h** and from the anilino donor to the adjacent dicyanocyclopentadiene acceptor in spiro compounds (\pm) -**3a**-**e**, as depicted in the molecular orbital representations of these levels (Tables 4SI and 11SI). Small but distinctive orbital overlaps in the cyclobutene moiety suggest that through-bond interactions are responsible for the intramolecular CT transition in cycloadducts (\pm) -**2a**-**h**.

The differences in intensity of the low-energy transitions between the series (\pm) -**2a**-**h** and (\pm) -**3a**-**e** are theoretically well predicted by the computed oscillator strengths *f*. While values of *f* range in the series of the non- π -conjugated chromophores (\pm) -**2a**-**h** from 0.053 to 0.109 (average 0.085), larger numbers in the range of 0.401–0.673 (average 0.564) are obtained in the conjugated push–pull chromophores (\pm) -**3a**-**e**. This can be explained by the enhanced electronic communication between the anilino donor and the dicyanocyclopentadiene moiety through C_{sp2}- π -conjugation in (\pm) -**3a**-**e** compared to the C_{sp3}homoconjugated chromophores (\pm) -**2a**-**h**.

Origin of the large difference in yields obtained in the thermal rearrangement

While spiro compounds (\pm) -**3a** and (\pm) -**3b** were obtained in high yield, derivatives (\pm) -**3c**-**e** were only isolated in poor yield (Table 2) and their formation, starting from the pure homoconjugated compounds (\pm) -**2c**-**e**, was accompanied by substantial amounts of insoluble, black decomposition products. Slow product decomposition in toluene at reflux is not responsible of the low yields obtained for (\pm) -**3c**-**e**. Also, there is no correlation between the electron-donor strength of the anilino substituents and the yields of the spirocyclic compounds.

DDQ is well known to oxidize *N*-alkylated anilines, leading to iminium ions via α -C_{sp3}–H abstraction,^[26] while anilines are also polymerized to polyanilines.^[27] In fact, reacting *N*,*N*-dimethylaniline with DDQ in dry toluene at reflux under N₂ produced an insoluble black-green solid within one hour. The reaction of *N*,*N*-diisopropylaniline was much slower and afforded an insoluble black film after 6 h.^[28] However, there was no reaction under the same condi-

tions when N,N-diphenylaniline was used as a substrate. We subsequently explored whether the homoconjugated [2+2] cycloadducts would undergo cycloreversion, thereby liberating DDQ which could then oxidize the aniline species present under formation of the undesired side products. In the literature, [2+2] cycloadducts obtained by via polar intermediates^[29, 30] have in fact been observed to undergo cycloreversion.^[31] We reacted the homoconjugated chromophores (\pm)-2a and (\pm) -4^[13] with TCNE in 1,2-dichloroethane at reflux (84°C) for 6 h and obtained by the thermal cycloreversion, followed by a [2+2] CA-RE reaction the anilino-substituted 1,1,4,4-tetracyanobuta-1,3-dienes (TCBDs) 5 and 6, respectively, in 41-42% yield, thereby confirming that cycloreversion indeed takes place (Scheme 2). No transformation was observed for the diphenylaniline derivative (\pm) -2b; in this case, only the spiro compound (\pm) -3 b formed in a very slow reaction. Cycloreversion also occurs in toluene at reflux (111 °C); here the formation of the spiro compounds is more competitive and starting from (\pm) -2a, TCBD 5 is obtained in 16% yield besides (±)-3a (40%). Starting from (±)-4, TCBD 6 forms in 12% yield besides the corresponding known^[13] spiro chromophore (18%).



Scheme 2. In situ trapping of the anilinoalkyne, formed by cycloreversion, with TCNE.

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Based on all these experimental findings, we propose that aniline species in the transformation to spiro derivatives (±)-**3 c**-**e** are oxidized by DDQ formed by the cycloreversion of the homoconjugated starting materials (±)-**2 c**-**e**. In contrast, such oxidation side reaction does not compete in the formation of the two spiro compounds (±)-**3 a**,**b**, that are formed in high yield (Table 2). Diphenylanilino species lack an α -C_{sp3}-H group and are not oxidized to iminium ions, whereas such oxidation is disfavored for diisopropylanilino species due to severe A1-3 strain in the iminium ions. Other, steric and thermodynamic stability arguments also cannot be dismissed. At this point, we cannot propose, which aniline species is actually oxidized by the DDQ^[28] liberated in the cycloreversion but the analysis above presumably holds for all of them.

Mechanistic studies by EPR spectroscopy

In our first report on the thermal rearrangement of homoconjugated (\pm)-**4** to the corresponding spiro compound, we proposed as the first step a conrotatory retroelectrocyclization to an eight-membered ring intermediate, which would subsequently have to be followed by a *cis/trans* isomerization to fur-

ther proceed with the rearrangement.^[13] While a corresponding free enthalpy reaction profile could be computed at the B3LYP/6-31 G(d) level with PCM solvation in toluene (see Figure 28SI), all attempts to model further reaction steps leading to the final spiro product were unsuccessful.

We believe that no ionic mechanism including any kind of transannular reactivity between the two carbonyl groups leads to the product. Modeling of many different possible transannular attacks, even stepwise, did not lead to any reasonable result. We concluded that a neutral biradical mechanism, which had actually been proposed by one of the reviewers of the earlier communication,^[32] is more likely and continued performing EPR studies.

The thermal rearrangement of the homoconjugated push-pull chromophores (\pm) -**2a**, (\pm) -**2b**, and (\pm) -**4** was investigated by EPR spectroscopy to inspect whether the reaction proceeds via open shell stages, that is, (bi)radicals or radical ions. Wellresolved EPR spectra with remarkable intensity were detected upon heating compounds (\pm) -**2 a**, (\pm) -**2 b**, and (\pm) -**4** in toluene under the exclusion of oxygen (Figure 4).

It was even possible to obtain a well distinguishable ENDOR spectrum revealing ¹H isotropic hyperfine coupling constants (hfcs, Figure 4d). The spectra displayed in Figure 4 cannot be obtained, when DMSO solutions of (\pm) -**2a**, (\pm) -**2b**, and (\pm) -**4** are treated in an analogous way. The analysis of the reaction in DMSO indicates cycloreversion of (\pm) -**2a** and (\pm) -**4** yielding DDQ and DAA-substituted acetylenes. The simulation of the EPR spectra shown in Figure 4 reveals two rather small ¹⁴N hfcs attributable to the amino nitrogen and one CN nitrogen atom and additional ¹H hfcs (Table 15SI). To test if these data correspond to electron-transfer-generated species, we selectively generated the radical anions and cations of (\pm) -**2b** and (\pm) -**4**.

Figure 5 displays the EPR spectra obtained upon electrolytic reduction of (\pm) -**2b** and (\pm) -**4** in THF. The spectral widths are small (ca. 0.5 mT) and the *g* factor of 2.0053 rather high (and similar to DDQ⁻),^[33] indicating that the spin and the charge are residing in the acceptor moiety of the molecule, as also reflected by the shape of the LUMO (Table 4SI).

Oxidation of (\pm) -**2b** and (\pm) -**4** with (bis(trifluoroacetoxy)io-do)benzene (PIFA) leads to EPR spectra clearly indicating an



Figure 4. EPR spectra (a–c) obtained upon heating of (\pm) -**2a**, (\pm) -**2b**, and (\pm) -**4** in toluene and the corresponding simulations. ENDOR spectrum (d) obtained upon heating of (\pm) -**2a** in diphenyl ether.



Figure 5. EPR spectra of a) (\pm)-**4**⁻⁻, g = 2.0053(1); b) (\pm)-**2**b⁻⁻, g = 2.0053(1), generated by electrochemical reduction in Ar-saturated THF solutions (0.1 \times *nBu₄NPF₆*) at 250 K.





amino-type radical cation, in which the predominate portion of the spin is concentrated at the amino nitrogen atoms and the directly adjacent substituents, corresponding to the HOMO of the parent molecules (Table 4SI). This is mirrored by the hyperfine data of (±)-2 b^{*+} and (±)-4*+ presented in Table 16SI. The size of the ¹⁴N hfcs in (\pm)-**2**b⁺ and (\pm)-**4**⁺ of approximately 0.9-1.0 mT are significant for triphenylamine and dimethylaminobenzene radical cations, respectively.^[34] This bears out that the EPR data representing the spectra obtained upon converting (\pm) -2a, (\pm) -2b, and (\pm) -4 to the corresponding spiro isomers do not stem from one-electron reduced or oxidized species. Remarkably, the multiplicities of the ¹H hfcs in Table 15SI are in line with species connected to (\pm) -2a, (\pm) -2b, and (\pm) -4. They can be tentatively related to a biradical species formed by homolytic cleavage of the most strained (CN)C-C(CN) bond between the fused four- and six-membered rings in the homoconjugated adducts. We therefore now tentatively propose the mechanism for the thermal rearrangement shown in Scheme 3.



Scheme 3. Proposed biradical mechanism for the thermal rearrangement of (±)-2 a–e to (±)-3 a–e. B and B': biradical intermediates.

Conclusion

A series of novel homoconjugated push-pull chromophores, (\pm) -**2a**-**h** with a central bicyclo[4.2.0]octane scaffold was obtained in high yield by [2+2] cycloaddition of DDQ to anilino-activated alkynes. In this series, the *N*-substituents on the aniline ring were systematically varied according to their electron-donation strength. Starting from (\pm) -**2a**-**e**, the thermal rearrangement to the π -conjugated spirocyclic push-pull systems (\pm) -**3a**-**e** was investigated, for which only a single example had been described in a previous communication.^[13] The structural and optoelectronic properties of the two new series of push-pull chromophores were investigated by comprehensive study, including X-ray analysis, UV/Vis spectroscopy, electrochemistry (CV and RDV), and computational analysis. The yields of the spirocyclic products (\pm) -**3a**-**e** in the thermal rearrange-

ment of the rather closely related homoconjugated systems (\pm) -2a-e differed rather strikingly. Whereas the bulkier N,N-diisopropyl ((\pm)-3 a) and N,N-diphenyl ((\pm)-3 b) derivatives were obtained in high yield, the three other compounds with pyrrolidino, didodecylamino, and dimethylamino residues were only formed in poor yield. It was then found by in situ trapping experiments with TCNE, that the homoconjugated adducts undergo cycloreversion under liberation of DDQ, which is known to oxidize N-alkylated anilines via C_{sp3}-H abstraction and formation of iminium ions. The low yields of (\pm) -3 c-e are most probably due to competing oxidation of aniline species by the DDQ formed in the cycloreversion. The high yields of (\pm) -3 a,b were explained by the absence of oxidation to an iminium ion in the case of the diphenylanilino derivative and by strain in the iminium ion that would be formed by the diisopropyl derivative. A mechanism for the thermal rearrangement initiated by retroelectrocyclization to an eight-membered ring and following cis/trans isomerization, which had been proposed in the earlier communication^[13] could not be further supported in DFT calculations of the free enthalpy reaction pathway. On the other hand, EPR investigations of the thermal rearrangement yielded well-resolved EPR spectra with remarkable intensity, suggesting that the reaction proceeds by open-shell biradical or radical ion species. Based on this finding, a biradical mechanism was proposed, as had already been suggested by one of the reviewers of the earlier communication.^[32]

Experimental Section

Only the general procedures for the synthesis of the target chromophores (\pm)-**2a**-**h** and (\pm)-**3a**-**e** are reported here, where as all other details and protocols can be found in the Supporting Information.

General procedure A (thermal [2+2] cycloaddition)

DDQ (1 equiv) was added under N_2 to a solution of electron rich alkyne (1 equiv) in 1,2-dichloroethane (20 mL). The mixture was stirred at 25 $^\circ C$ for 30 min and the solvent removed in vacuo. The residue was purified by FCC to give homoconjugated chromophore.

General procedure B (thermal reaarangement)

A solution of homoconjugated chromophore (100 mg) in dry toluene (250 mL) was heated to reflux for 5–24 h. The solvent was removed in vacuo. Dichloromethane was added to the residue and the mixture stirred vigorously for 10 min. Insoluble material was removed by filtration, and the filtrate was evaporated in vacuo. The residue was purified by FCC to give spiro compound.

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