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Selective Even-Numbered Bromination of Triptycene Tris(thiadiazoles)

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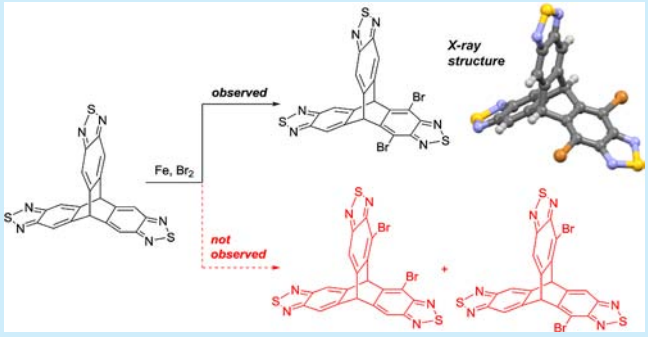
Supporting Information

ABSTRACT: An unusual even-numbered bromination of triptycene tristhiadiazole is described, giving selectively dibromo-, tetrabromo-, and hexabromotriptycenes with two bromines each at the same phenyl ring. The new compounds can be used as precursors for extended π-conjugated systems and polymers.



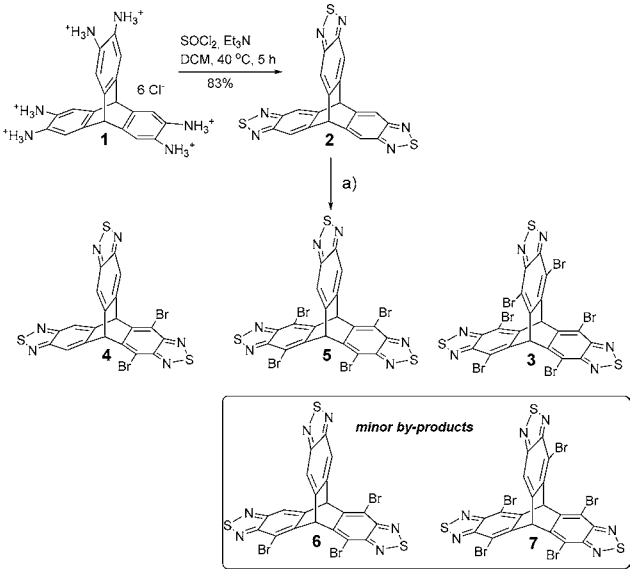
The 2,1,3-benzothiadiazole moiety is frequently used as an electron-withdrawing unit in conjugated polymers or discrete organic molecules to lower the LUMO of the material and therefore broaden the light absorption properties of conjugated polymers bathochromically to harvest more sunlight. Indeed, this molecular motif is part of some of the best performing donor polymers and defined compounds embedded in bulk heterojunction organic solar cells.[1,2] From a synthetic point of view, the benzothiadazole unit is often dibrominated in the ortho-positions to functionalize it for subsequent cross-coupling reactions. Usually, the dibromination is performed by HBr/Br_2 with almost quantitative yields,[3] but also under harsher conditions, as has been reported for electron-poor 3,4-difluoro-substituted benzothiadiazoles.[4]

During our ongoing research on extending the aromatic π-planes of triptycenes on the basis of triptycene hexaammonium salt **1**,[5−7] we planned to synthesize the corresponding trisbenzothiadiazole **2** and subsequently transform it into the 6-fold brominated congener **3** (Scheme 1) for further derivatizations. Here, we describe the observation of an unusual substitution pattern at the triptycene through direct bromination reactions, giving selectively even-numbered brominated products, which are themselves valuable precursors for versatile further transformations, e.g., by cross-coupling reactions to give conjugated polymers on the basis of triptycene.[8]

The first step of the synthesis was the transformation of the hexaammonium salt **1** into the trisbenzothiadiazole (TBTDA) **2** by refluxing a mixture of **1**, thionyl chloride, and triethylamine in DCM for 5 h, giving TBTDA **2** in 83% yields.[9]

Single crystals of TBTDA **2** of high quality have been grown by sublimation at 300 °C and 1.2 mbar. The molecules self-assemble via weak hydrogen bonding[10] of two adjacent molecules and $\pi-\pi$-stacking[11] (Figure 1 and Supporting Information). The lengths of the C−C-bonds of the phenylene rings are not similar. For instance, the bonds between C22 and C23 as well as between C21 and C26 are with 1.36 Å significantly shorter than the remaining four C−C bonds in the ring (d(C23−C24) = 1.42 Å, d(C24−C25) = 1.43 Å, and d(C21−C22) = 1.44 Å), suggesting a more olefinic than

Scheme 1. Synthesis of Brominated Trisbenzothiadiazoles[a]



[a]For reaction conditions and yields, see Table 1.

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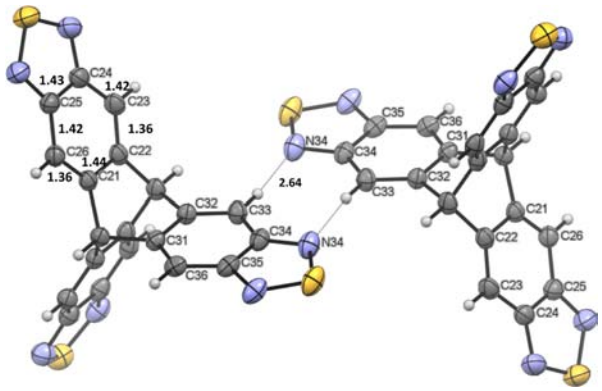

Figure 1. X-ray crystal structure analysis of TBTDA **2**. Depicted is a dimer via weak hydrogen bonding between two adjacent molecules and the bond lengths of a representative benzothiadiazole ring. Probability of ellipsoids is 50%.

aromatic character of the two bonds between C21 and C26 as well as C22 and C23 (see also discussion below).

After **2** was reacted with 150 equiv of bromine and 12 equiv of iron powder at 40 °C for 14 h, the crude product was analyzed by UPLC MS (Supporting Information): three main products have been formed with m/z values of the basis peaks of 586.00, 743.82, and 901.64, which correspond to a 2-fold, 4-fold, and 6-fold bromination of triptycene **2**. After the main products were separated by column chromatography, we found that each aromatic benzothiadiazole unit is either dibrominated or nonsubstituted, giving the products **4** (31%), **5** (15%), and **3** (traces) in addition to recovered thiadiazole **2** (34%). However, the amount of bromine can be reduced to 34 equiv and the reaction time to 2 h, giving an even higher selectivity of **4** (32% yield) when upscaled from 0.12 to 0.94 mmol. To achieve the hexabromotriptycene **3** under similar reaction conditions, a large excess of bromine (600 equiv) and a higher loading of iron powder (12 equiv) was necessary to give at 55 °C and 140 h **3** as main product in 67% yield besides 9% of tetrabromotriptycene **5**. With HBr and Br_2, a nearly full conversion of **2** to **3** can be achieved with a much lower stoichiometry of bromine (50 equiv), after heating the mixture 24 h at 140 °C in a closed screw-capped vessel, giving **3** in 94% isolated yield. A similar result can be achieved with $FeCl_3 \cdot 6H_2O$ instead of HBr under milder conditions (55 °C), giving 97% of **3**, even on a larger scale (4.2 mmolar). It is worth mentioning that with anhydrous $FeCl_3$ under the same conditions the reaction does not run to completion and gives again the typical pattern of products with even-numbered brominations, as observed for the reaction with Fe/Br_2.

Other regioisomers of **4** and **5** could be excluded by analysis of the ^1H NMR spectra. For example, for **4**, only two singlets have been observed at δ = 8.16 ppm with integral 4H and δ = 6.38 ppm (2H), which can be assigned to the aromatic protons and the bridgehead protons, respectively. For the possible regioisomer **4a** depicted in Figure 2, two signals in the aromatic region and one signal for the bridgehead protons are expected, each of integral 2H. For **4b**, it would be three signals of the aromatic protons (with integrals 1H, 1H, 2H) and two signals for the bridgehead protons (each 1H). Both signal patterns have not been observed.

Besides NMR characterization, a single-crystal X-ray structure analysis of dibromotriptycene **4** is clear proof of the proposed structure (Figure 3). The molecules are packed via

Table 1. Reaction Conditions and Yields of Bromination of TBTDA 2

	reaction conditions[a]			isolated yields (%)			
entry	additive (equiv)	Br_2 (equiv)	time (h); temp (°C)	**2**	**4**	**5**	**3**
1	Fe (12)	150	14; 40	34	31	15	*b*
2[c,d]	Fe (6)	34	2, 55	18	32	18	6
3	Fe (12)	600	140; 55			9	67
4	HBr	50	140; 24				94
5[e]	$FeCl_3 \cdot 6H_2O$ (6)	50	55; 26				97

[a]For exact conditions, see the Supporting Information. [b]Approximately 7% of hexabromtriptycene **6** has been formed, but here not isolated and purified. [c]2% of tribromotriptycene **5** has been additionally isolated. [d]0.94 mmolar scale. [e]0.7 mmolar scale.

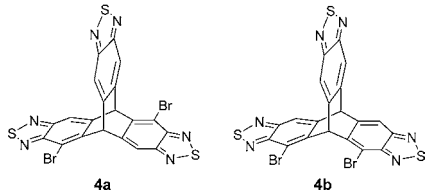

Figure 2. Possible regioisomers of dibromotriptycene **4**.

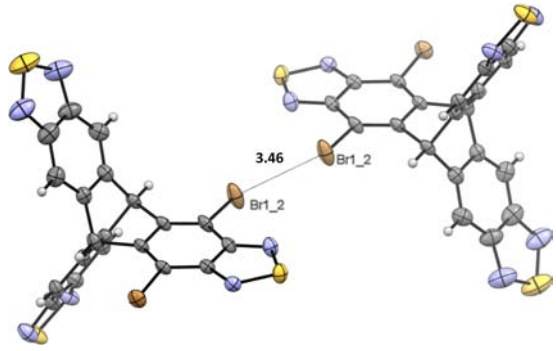

Figure 3. X-ray crystal structure of dibromotriptycene **4**. Depicted are two molecules interacting via halogen−halogen bonding. Probability of ellipsoids is 50%. Enclathrated solvent molecules are omitted for clarity.

halogen bonding,[12a] halogen−halogen bonding[12b] between the bromo substituents of adjacent molecules (d(Br···Br) = 3.46 Å), pnicogen interaction[13] of S and N in a dimeric cyclic fashion (d(S···N) = 3.07 Å), and weak $\pi-\pi$-stacking (d = 3.79 Å) (see the Supporting Information).

To the best of our knowledge, there are only a few reports of brominating compounds that contain more than one benzothiadiazole unit, where both the 4- and 7-position of the benzothiadiazole units are not substituted.[14−17] Only in one case was a 2-fold bromination of only one of the two present benzothiadiazole cores reported.[14] Although a clear structural proof has been made that only one BTDA unit was brominated, no further suggestion on the mechanism was given.[14] If an electrophilic aromatic substitution mechanism for the bromination is assumed (see Scheme 2, left path), it is more likely that after addition of the first bromine substituent at the BDTA unit the electron density of the aromatic phenyl ring is decreased and in comparison to the other two still nonsubstituted BDTA units in the triptycene should be less likely attacked by the electrophile, expecting a product mixture of **4a**

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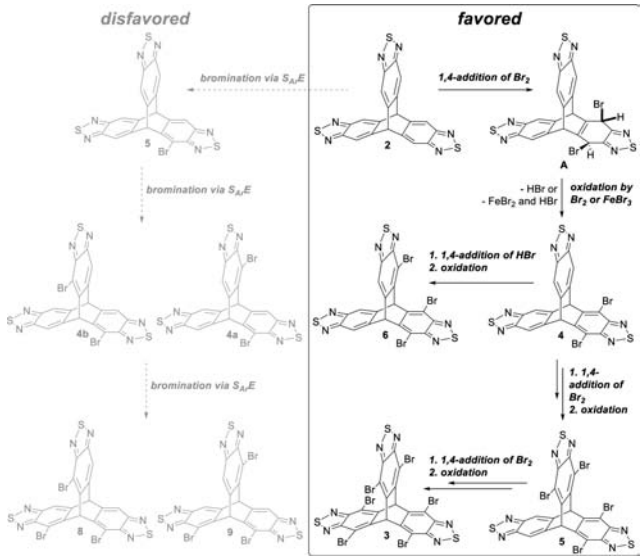
Scheme 2. Proposed Mechanism for the Selective Even-Numbered Bromination

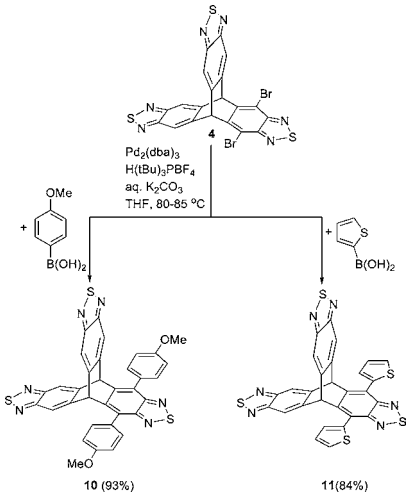


and **4b** for the second bromination step, which is obviously not observed.

To explain the even-numbered bromination of each ring, it is suggested that, according to the X-ray single crystal structure of **2**, the C−C bond lengths of the phenyl rings are alternating and hence are more of olefinic than aromatic character, which would explain the 1,4-addition as a favored reaction.[3] As a mechanistic rationale it is proposed that 1,4-addition of Br_2 is occurring first (Scheme 2, right path), introducing both bromine substituents at one ring at a time, giving intermediate **A**, followed by a subsequent rearomatization of the phenylring via oxidation, either by bromine itself (E_{red} = +1.09 eV) or by $FeBr_3$ (E_{red} = +0.77 eV) giving dibromotriptycene **4**. As mentioned above, no other regioisomers of dibrominated triptycenes such as **4a** and **4b** could be observed or isolated, assuming that this 1,4-addition−oxidation sequence is favored over a competitive (multiple) electrophilic aromatic substitution sequence. The formation of tetrabromide **5** and hexabromide **3** can be explained by a repetition of the 1,4-addition−oxidation sequence with compound **4** or **5**, respectively. By UPLC−MS the formation of minor byproducts, with m/z values of 663.74 and 821.95 of tribromo- and pentabromo-substituted triptycenes, can be detected. We were able to isolate the 3-fold brominated triptycene **6** (2%) and confirmed the structure by NMR methods, again excluding the formation of the other regioisomeric tribromotriptycenes **8** and **9**. Those minor byproducts **6** and **7** are probably formed by the competitive addition of HBr, which is the product of the oxidation process, instead of Br_2. Alternatively, slow elimination of HBr from the Br_2 addition product, as observed for anthracenes,[18] could be responsible for the small amount of this byproduct. Until now, first attempts at isolating the aliphatic dibrominated intermediate **A** were not successful to fully prove the proposed mechanism and will be further pursued in the future.

The even brominated triptycenes **3** and **4** are attractive precursors, e.g., for small nonplanar and D_{3h}-symmetric electron-acceptors[19] or triptycene-based conjugated polymers with IMFV.[8] As a model reaction for the synthesis of conjugated polymers by Suzuki−Miyaura cross-coupling, dibromotriptycene **4** was reacted with *p*-anisylboronic acid and 2-thienylboronic acid to give the products **10** and **11** in high yields of 93% and 84%, respectively (Scheme 3). Both compounds could be additionally characterized by single-crystal X-ray structure analysis (see also the Supporting Information).

Scheme 3. Suzuki−Miyaura Cross-Coupling Reactions of Dibromotriptycene 4



All compounds have been characterized by UV/vis and fluorescence spectroscopy as well as by cyclovoltammetry (see Table 1, Figure 4, and the Supporting Information). In the UV/vis spectra all compounds show a pronounced maximum between λ = 332 and 336 nm. More interesting for the bromosubstituted compounds **3**−**5** is that with increasing number of bromine substituents, well-structured weak peaks are appearing bathochromically to the maximum, with increasing intensities. Those peaks are probably from n−π^* transitions from lone pairs of the bromine substituents to the π^* orbitals. The cross-coupled products **11** and **12** show in the UV/vis due to the elongated π-system additional peaks at λ = 372 and 387 nm, respectively. With increasing number of bromine substituents, the energies of the LUMOs are lowered from E_{LUMO} = −2.9 eV for the nonsubstituted triptycene **2** to −3.2 eV for the hexabrominated compound **3**, whereas the energies of the HOMOs are raised by aryl substituion from −6.5 eV to −5.8 or −5.7 eV for compounds **10** and **11**.

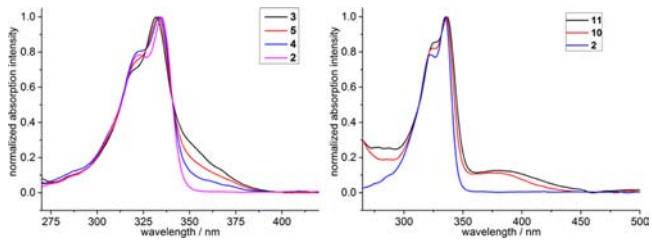


Figure 4. UV/vis absorption. For detailed data, see Table 2.

To summarize, for the direct bromination of BDTA **2** an unusal even-numbered substitution pattern was found giving the di-, tetra-, and hexabromotriptycenes **4**, **5**, and **3** selectively. To the best of our knowledge, only 1,4-dibromotriptycenes have been described to date, which require multiple synthetic steps.[20] Further investigations will elucidate the mechanism.

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Table 2. Summary of Photophysical and Electrochemical Characterization of All New Compounds

compd	λ_{max} [a] (ε) (nm) [(M^{-1} cm^{-1})]	λ_{em} [a] (λ_{ex}) (nm)	$E_{g(opt)}$ [b] (eV)	$E_{1/2\ red}$ [c,d] (V)	E_{LUMO} [e] (eV)	E_{HOMO} [f] (eV)
2	335(84844)	373 (325)	3.6	−1.9	−2.9	−6.5
4	334(78319)	415 (324)	3.3	−1.7	−3.1	−6.4
5	333(70578)	412 (323)	3.2	−1.6	−3.2	−6.4
3	332(66259)	419 (322)	3.2	−1.6	−3.2	−6.4
10	336(16820)	513 (326)	2.8	−1.9	−3.0	−5.8
11	336(16820)	541 (326)	2.7	−1.9	−3.0	−5.7

[a]Measured in $CHCl_3$ at rt. [b]Estimated from absorption onset. [c]Measured in THF with NBu_4PF_6 as electrolyte. [d]Calculated against the internal standard for Fc/Fc^+. [e]$E_{LUMO} = -(E_{1/2(red)} + 4.8\ eV)$. [f]$E_{HOMO} = E_{LUMO} - E_{g(opt)}$.

The brominated compounds will be used for the synthesis of π-conjugated polymers of intrinsic microporosity and small electron acceptors.[19,21,22]

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and analytical data of all new compounds, NMR spectra, and crystal structure information files of **2**, **4**, **10**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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