Proving Triptycene Homoconjugation with the Same Chromophore but Different Connectivity to the Core

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Dedicated to Prof. Dr. Peter Bäuerle on the Occasion of his 65th Birthday.

Introduction

Homoconjugation is an effect influencing the electronic properties of molecules by “through space” orbital interactions. 1, 2 In this respect, especially triptycene was investigated in depth 1, 3 and already early reports describe spectroscopic differences between triptycene and triphenylmethane, which can only be explained by homoconjugation effects. 5 It was in 1983 when Martin et al. used photoelectron spectroscopy in combination with theoretical calculations to finally prove the existence of homoconjugation. 6 These findings have been picked up more recently by studies on dialkoxytriptycenes and their oxidations to the corresponding quinones by Rathore and coworkers in solution and in silico. 7 Additionally, empirical results such as the possibility to monosubstitute triptycene in electrophilic aromatic substitution reactions, such as nitration, rather than obtaining statistical mixtures of mono-, di-, and trisubstituted triptycenes underline the assumption of an electronic communication between the triptycene paddles, influencing the reactivity of each other. 8 – 10 Recently, a series of 15 triptycene derivatives with different donor and acceptor moieties has been reported, clearly showing how homoconjugation influences the donating or accepting nature of identical acceptor and donor units depending on their number. 11

With the exception of the photoelectron spectroscopic evidence of the homoconjugation for unsubstituted triptycene, 6 all other contributions rely on either different π-systems which are connected via the bicyclic core 1, 4, 11, 12 or comparing different twofold substitution patterns (ortho- or para-dimethoxy triptycenes) and their oxidation behavior. 7 Rathore et al. calculated possible homoconjugation of a variety of structurally related triptycenes with enlarged π-blades or better chromophores on the bicyclic backbone with the outcome that subtle structural changes can have a significant impact on homoconjugation effects. 7 However, they came to the conclusion that the nodal arrangement of the HOMO orbital coefficients found at the closest atoms of the core can be used to define the amount of homoconjugation. 7

To the best of our knowledge, homoconjugation has not been investigated for constitutional isomers having the same chromophore (Figure 1) just connected in a different way to the bicyclic core, which is presented herein. The chromophore 13 used in this study is attached either at the thienoquinoline unit (Figure 1, red dots) or at the phenol ring (Figure 1, blue dots) to the 2-, 3-, 5-, 6-, 7-, and 8-positions of the bicyclo[2.2.2]octane core.

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Results and Discussion

The synthesis of the triptycene-based thienoquinoline 8 started from trisamido triptycene 2,9,10,14 which was threefold brominated (NBS, DMF) to give triptycene 3 in 88% yield (Scheme 1).15 After acidic amide cleavage (HCl, EtOH), triamino, tribromo triptycene 416 was isolated in 97% yield. Subsequent Suzuki–Miyaura cross-coupling with the hexyl-substituted thiophene boronic acid ester 517 under Fujita conditions (Pd2dba3, HBF4Et2O)18 gave 86% of triptycene 6 after purification (Scheme 1).

Triamino, triaryl triptycene 6 was reacted with di-tert-butylsalicylaldehyde 7 under Pictet–Spengler conditions [PhMe, TFA (10 mol%), O2, 100 °C, 3 h]19,19 to finally give 8 in 55% yield after recrystallization from a chloroform/ethanol mixture (Scheme 2). The synthesis of the structural isomer20 11 was achieved also by a threefold Pictet–Spengler reaction. Here, triptycene tris-salicylaldehyde 921 was reacted with ortho-hexylthieno aniline 10 (for details on the synthesis, see the Supporting Information) under the aforementioned conditions.
conditions. After precipitation from dichloromethane and washing with n-pentane, 11 was isolated in 45% yield. All obtained triptycene derivatives have been fully characterized (see the Supporting Information) and the structure of triamino, tribromo triptycene 4 was unambiguously proven by single-crystal X-ray diffraction (Figure 2).

Triptycenes 8 and 11 were examined by UV/vis spectroscopy in chloroform and the obtained results were compared with model compound 1, representing one isolated chromophore of the other two (Figure 3). For 1 a highest wavelength absorption maximum at $\lambda_{abs} = 364$ nm and additional maxima at $\lambda_{abs} = 311$ nm and $\lambda_{abs} = 272$ nm were observed. Triptycene 11 shows a comparable highest wavelength absorption at $\lambda_{abs} = 363$ nm and an additional maximum at $\lambda_{abs} = 308$ nm, as well as a shoulder at $\lambda_{abs} = 265$ nm. In contrast to 1 and 11, triptycene 8 has a bathochromically shifted ($\Delta \lambda = 13$–14 nm) longest wavelength absorption at $\lambda_{abs} = 377$ nm. Furthermore, a maximum of high intensity at $\lambda_{abs} = 272$ nm makes a clear spectroscopic difference for 8 and 11. Since both compounds have the same chromophore, this difference is assigned to homoconjugation effects rather than inductive effects of the two tert-butyl substituents found in 8.22

To get a deeper understanding of the electronic properties of the three compounds, for the aromatic backbones of 1, 8 and 11, models without alkyl substituents (denoted as 1', 8', and 11') have been investigated by dispersion-corrected (GD3BJ) density functional theory (DFT) calculation [B3LYP-6-311(d,p); Figure 4].23 For model compound 1', the HOMO energy level is found at $E_{\text{HOMO}} = -5.90$ eV with the largest atom orbital coefficients at the phenolic substructure. Nevertheless, the HOMO is also distributed over the thienoquinoline part of the molecule (Figure 4, left). The corresponding LUMO can be found delocalized over the whole molecule, here the main proportion of orbital coefficients is found at the thienoquinoline unit. The energy level is at $E_{\text{LUMO}} = -2.11$ eV, resulting in a gap of $\Delta E_{\text{HOMO-LUMO, DFT}} = 3.79$ eV.

For triptycene 8' bearing three of those chromophores, the HOMO energy is destabilized by $+0.09$ eV ($E_{\text{HOMO}} = -5.81$ eV) in comparison to 1'. In contrast, the degenerated LUMOs are stabilized by $-0.14$ eV ($E_{\text{LUMO}} = -2.25$ eV) and the HOMO–LUMO gap is slightly decreased to $\Delta E_{\text{HOMO-LUMO, DFT}} = 3.56$ eV. This destabilization in HOMO energy of the triptycene vs. the monomeric chromophore of about 0.1 eV is in agreement with Rathore et al.'s suggestion.7 Furthermore, the nodal arrangement of HOMO coefficients is comparable to all compounds, where homoconjugation was suggested to be found (Figure 5).7

More interesting than comparing model compound 1' with triptycene 8' is the comparison of the two isomeric triptycenes 8' and 11'. In contrast to 8', the HOMO coefficients of 11' are located on the phenol units exclusively, whereas those of the LUMO are delocalized over the whole backbones of the chromophore units (Figures 4 and 5). For 11', both HOMO and LUMO are destabilized by $+0.28$ eV ($E_{\text{HOMO}} = -5.53$ eV) or $+0.40$ eV ($E_{\text{LUMO}} = -1.85$ eV) in comparison to 8'. The resulting $+0.12$ eV larger HOMO–LUMO energy gap of $\Delta E_{\text{HOMO-LUMO, DFT}} = 3.68$ eV is in agreement with the observations made using UV/vis spectroscopy (see above).
According to the assumptions made by Rathore and coworkers, the HOMO destabilization of 11 to model compound 1 is about 370 meV, which is one of the largest values found for triptycene-based systems.7

Cyclic voltammetry (CV) investigations (Figure 6) of compounds 1 and 8 show comparable oxidation potentials of $E_{\text{ox, onset}} = 0.51 \text{ V (1)}$ and $E_{\text{ox, onset}} = 0.47 \text{ V (8)}$ with a slightly lower ($-0.04 \text{ V}$) potential for triptycene 8, which is in agreement with the observed small destabilization of the HOMO found by DFT calculations (see above). While 1 shows one distinct quasi-reversible oxidation wave, the oxidation processes of triptycene 8 are less defined, suggesting an additional oxidation process at higher potentials overlapping with the first oxidation wave.11,24 Unfortunately, the solubility of the isomer 11 was too low to gain more information on homoconjugation effects by CV.

**Conclusions**

In summary, two triptycenes with the same π-extended chromophores yet differently attached to the bicyclic core have been synthesized and compared to a model compound representing one triptycene paddle. The triptycene where the chromophore is attached at the phenolic substructure shows comparable spectroscopic (UV/vis) behavior to the model compound. The attachment at the thienoquinoline unit leads to a bathochromic shift of $\Delta \lambda = 13 \text{ nm}$ of the lowest energy absorption which can be attributed to homoconjugation
effects. DFT calculations [B3LYP-6-311(d,p) with GD3BJ
dispersion correction] underline the assumption that
the degree of homoconjugation is dependent not only
on the nature of the extended aromatic paddle but also on the
attachment site due to differences in orbital interaction. These
findings clearly demonstrate that electronic and optical
properties in three-dimensional
π-extended molecules can be fine-tuned without changing the chromophoric structure
by itself, but rather by varying the orientation of chromo-
phores in space. This opportunity expands the toolbox of
chromophore design to another dimension. The here-
described triptycenes 8 and 11 can be used as threefold
bidentate N,O-ligands, e.g. for BF₂-complexes,¹³ which are
under investigation in our laboratory.

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Supporting Information
Supporting Information for this article is available online at:

References And Notes

Figure 5 Zoom-in on the HOMOs of compounds 8′ (a and b) and 11′ (c and d) around the bicyclo[2.2.2]octane core calculated by dispersion-
corrected (GD3BJ) DFT methods (B3LYP-6-311(d,p)).

Figure 6 Cyclic voltammograms of model compound 1 and triptycene 8 in CH₂Cl₂ using nBu₄PF₆ (0.1 M) as the electrolyte with a Pt electrode
and Fc/Fc⁺ as the internal reference (scanning speed: 100 mV s⁻¹).
(20) The structural isomerism is only referred to the chromophoric units and the central triptycene. The tert-butyl units of 11 are to be neglected in this respect, yet had to be introduced due to solubility reasons.