

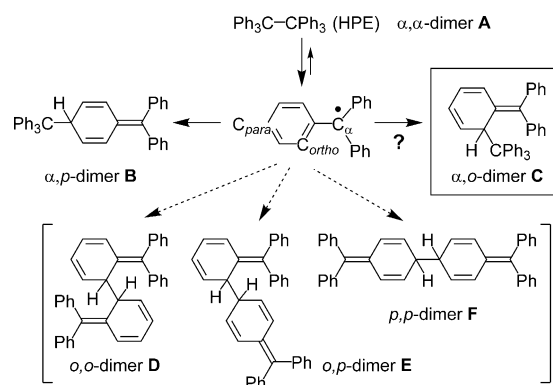
New Insights into the Hexaphenylethane Riddle: Formation of an α,α -Dimer**

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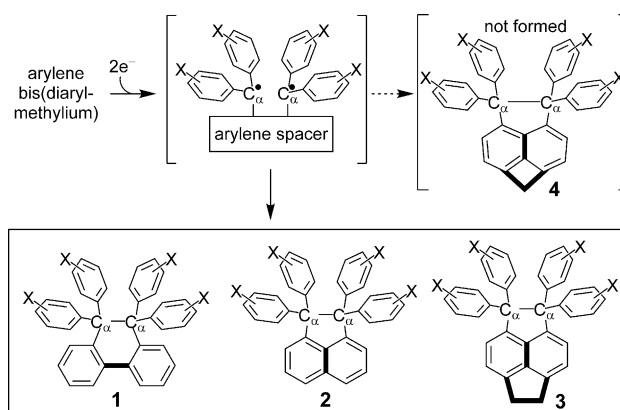
Dedicated to Prof. Yoshiro Yamashita

Abstract: Upon reduction of a 1*H*-cyclobuta[de]naphthalene-4,5-diylbis(diarylmethyl) species, a new C–C bond is formed between the C_α and C_{ortho} atoms of the two chromophores, which presents an unprecedented coupling pattern for the dimerization of two trityl units. By attaching an annulated cyclobutane ring at the opposite *peri* position of the naphthalene core, the distance between the C_α carbon atoms was elongated beyond the limit of σ -bond formation through “scissor effects”. The suppression of C_α – C_α bond formation, which would lead to hexaphenylethane-type compounds, is key to the first successful isolation of the α,α -adducts. The 5-diarylmethylene-6-triarylmethyl-1,3-cyclohexadiene unit in the α,α -adducts is stable, and isomerization of the cyclohexadiene unit into an aromatic system was not observed. The newly formed C_α – C_{ortho} bond was cleaved upon two-electron oxidation to regenerate the dicationic dye.

Hexaphenylethane (HPE, **A**) is a molecule with many riddles.^[1] The trityl radical ($\text{Ph}_3\text{C}^\bullet$) dimerizes to form 3-diphenylmethylene-6-triphenylmethyl-1,4-cyclohexadiene (α,α -dimer, **B**),^[2] as **B** is thermodynamically more stable than **A** (α,α -dimer), and the central C–C bond of **A** is easily cleaved to regenerate two radicals (Scheme 1). When the formation of the α,α -dimer is prevented by the attachment of bulky substituents on the aryl moieties, HPE derivatives (α,α -dimers) can be generated,^[3] which also gain stability by dispersion forces.^[4] The “arylenediyl” approach^[5] is another method for facilitating α,α -coupling. By connecting or annulating two phenyl groups between the two radicals, the C_α carbon atoms are spatially arranged in close proximity, and the formation of a C_α – C_α bond becomes a favored intramolecular process (Scheme 2). Thus, a series of 9,9,10,10-tetraaryl-9,10-dihydrophenanthrenes **1**^[6] or 1,1,2,2-tetraaryl-acenaphthenes **2**^[7] were prepared as stable α,α -adducts^[8]



Scheme 1. Dimerization modes of the trityl radical.



Scheme 2. Arylenediyl approach for facilitating α,α -couplings.

despite their elongated C_α – C_α bond with a length of up to 1.708(4) Å^[10a] (standard bond length: 1.54 Å).

Other coupling modes for a trityl radical, such as α,α -, α,α -, and p,p -dimerization,^[12] are energetically disfavored because a greater number of aromatic sextets^[13] are lost in the resulting dimers (**D–F**) than in **A** or **B**. In this context, the α,α -dimer (**C**), which has the same number of aromatic sextets as **B**, is especially interesting. Considering that **B** and **C** have nearly the same steric energy ($\Delta E = 6.63 \text{ kcal mol}^{-1}$) as estimated by calculations employing the OPLS force field (Supporting Information, Figure S1),^[14] there should be no reason for the absence of α,α -adducts, although such derivatives have never been described in the literature. As HPE derivatives (α,α -adducts) become accessible when the α,α -coupling is suppressed, the α,α -adducts should be generated

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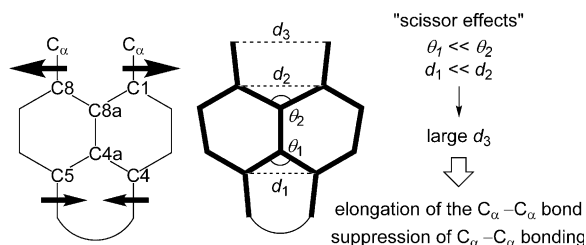
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when the formation of the corresponding α,p - and α,α -adducts is prevented.

We planned to suppress the α,p -coupling by adopting the arylenediyl approach using a naphthalene-1,8-diyl skeleton as in **2**. The C_α and C_{ortho} carbon atoms of each radical unit are thus brought into close contact in addition to the two C_α atoms. "Scissor effects" through ring annulation at the opposite *peri* position of the naphthalene core were then considered (Scheme 3). The angle strain induced by annula-

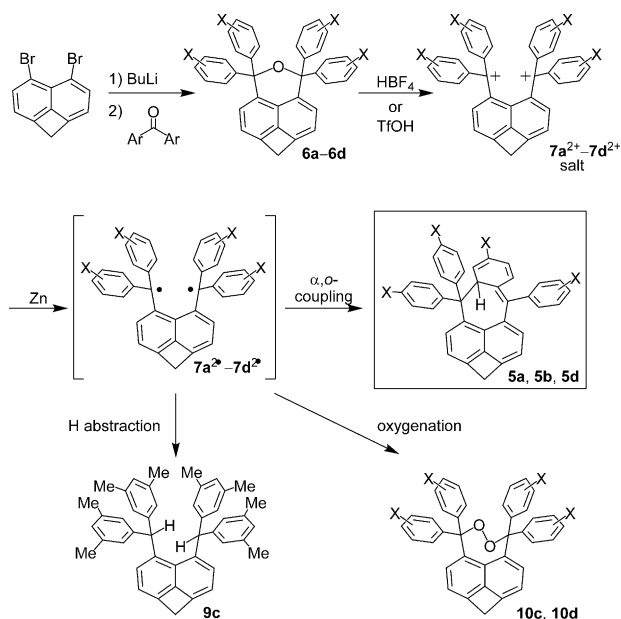


Scheme 3. Scissor effects in a naphthalene core fused to another ring system at the opposite *peri* position.

tion of a five-membered ring, as in 1,1,2,2-tetraarylpyracenes **3**, would result in a smaller θ_1 angle and a larger θ_2 angle so that the interatomic distance d_2 becomes much greater than d_1 . In 4,4,5,5-tetraaryl-1*H*-cyclobuta[*fg*]acenaphthenes **4**, these effects would be more prominent and prevent $C_\alpha-C_\alpha$ bonding because the interatomic distance d_3 is much greater in the precursor diradicals for **4** than in those for **3**.

In fact, we found that a series of compounds **3**, which display such scissor effects, have a longer $C_\alpha-C_\alpha$ bond [up to 1.761(4) Å]^[10b] than **2**. Furthermore, the same pyracene skeleton made it possible to observe the longest C–C bond [1.791(3) Å]^[11] in the di(spiroacridan) derivative.^[15] On the other hand, a DFT calculation for **4a** (X = H) predicted a $C_\alpha-C_\alpha$ bond length of 1.813 Å (Figure S2),^[16] which is much greater than the distance reported for the shortest non-bonded contact [1.80(2) Å].^[17] Thus, it is highly likely that in 1*H*-cyclobuta[*de*]naphthalene-4,5-diyl diradicals, both the α,p - and α,α -coupling pathways would be suppressed so that α,o -adducts can be obtained for the first time. Herein, we report the successful generation and isolation of α,o -adducts **5** along with their unique properties and X-ray structures.

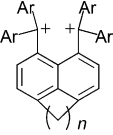
The reaction of 4,5-dibromo-1*H*-cyclobuta[*de*]naphthalene^[18] with BuLi in diethyl ether followed by the addition of benzophenone gave pyran **6a**^[19] (66% yield) after acidic workup with trifluoroacetic acid (Scheme 4). The 4-fluoro-, 3,5-dimethyl-, and 4-methoxy-substituted derivatives (**6b–6d**)^[19] were similarly obtained in yields of 59, 81, and 85%, respectively. Upon treatment of pyrans **6a–6c** with TfOH in a mixture of (CF₃)₂CHOH and CH₂Cl₂, the dication **7a**²⁺–**7c**²⁺ were generated, and their crude (TfO[–])₂ salts were directly used for the next step after removal of the solvents in vacuo. For a substrate with electron-donating methoxy groups, namely pyran **6d**, the dication was more easily generated with HBF₄ in a mixture of trifluoroacetic anhydride and CH₂Cl₂, and **7d**²⁺–(BF₄[–])₂^[19] was isolated in 94% yield as stable red crystals, which were suitable for X-ray crystallography (Figure S3).



Scheme 4. The α,o -adducts **5** were generated by reduction of dication **7**²⁺ along with several side products. **a**: X = H; **b**: X = 4-F; **c**: X = 3,5-Me₂; **d**: X = 4-OMe.

The geometrical parameters that were determined by X-ray analysis at 150 K^[20] clearly show that scissor effects are prominent in the cyclobutanaphthalene skeleton of **7d**²⁺ (Table 1).^[21] Therefore, the difference between the angles θ_1 and θ_2 is more than 40°, and d_2 is greater than d_1 by 0.62 Å.

Table 1: Geometrical parameters related to the scissor effects determined by X-ray analysis at 150 K.

Parameter ^[a]	7d ²⁺ ^[b]	8d ²⁺ (A) ^[c]	8d ²⁺ (B) ^[c]	
θ_1 [°]	96.6(4)	112.0(7)	112.2(7)	
θ_2 [°]	137.9(4)	128.6(7)	128.6(7)	
d_1 [Å]	2.071(7)	2.348(18)	2.339(18)	Ar = 4-MeOC ₆ H ₄
d_2 [Å]	2.695(6)	2.608(17)	2.595(16)	7d ²⁺ : n = 1
d_3 [Å]	3.396(7)	3.143(16)	3.177(16)	8d ²⁺ : n = 2

[a] For the definitions, see Scheme 3. [b] In **7d**²⁺–(BF₄[–])₂. [c] In **8d**²⁺–(BF₄[–])₂–CH₂Cl₂ with two crystallographically independent molecules A and B.

Whereas a similar in-plane deformation was also observed in the crystal structure of acenaphthene-5,6-diylbis(diarylmethyl) salt **8d**²⁺–(BF₄[–])₂,^[20] the effects are much less pronounced in this five-membered-ring analogue. Consequently, the non-bonded $C_\alpha-C_\alpha$ separation in **7d**²⁺ [d_3 = 3.396(7) Å] is much longer than in **8d**²⁺ [3.143(16), 3.177(16) Å]. The increase in d_3 by more than 0.2 Å would be enough to suppress the $C_\alpha-C_\alpha$ coupling pathway in the diradicals derived from **7**²⁺ whereas the reduction of **8**²⁺ was shown to be a reliable method for the synthesis of compounds **3**, which feature a long $C_\alpha-C_\alpha$ bond.^[11,22] On the other hand, because of the $C_\alpha-C_{ortho}$ distances of 3.251(7) and 3.282(7) Å in **7d**²⁺, we hypothesized that a new C–C bond-forming

process between these two carbon atoms should be possible upon reduction of 7^{2+} .

When a MeCN solution of $7a^{2+}-(TfO^-)_2$ was treated with Zn dust under argon atmosphere, yellow crystals with a molecular formula of $C_{37}H_{26}$ were obtained as the sole product (63 % yield over two steps). 1H and ^{13}C NMR spectra indicated the presence of a methine and a conjugated triene unit, suggesting the successful formation of α,o -adduct **5a**^[19] (Scheme 4). Similarly, reduction of 4-fluorophenyl derivative $7b^{2+}-(TfO^-)_2$ gave yellow crystals of **5b**^[19] (85 % yield over two steps); their structural identity was unambiguously confirmed by X-ray analysis (Figure 1).^[20]

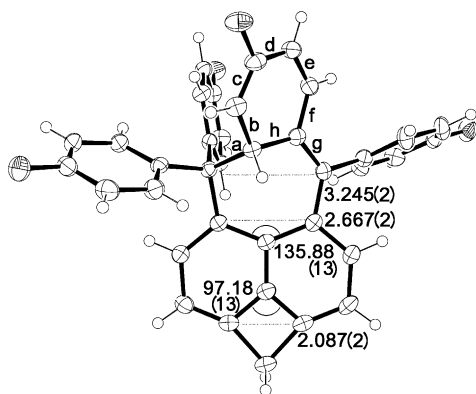


Figure 1. Molecular structure of α,o -adduct **5b** determined by X-ray analysis at 150 K. Selected bond lengths [Å]: a 1.6155(14), b 1.516(2), c 1.325(2), d 1.453(3), e 1.338(3), f 1.458(2), g 1.359(3), h 1.530(2).

The cyclobutanaphthalene unit also exhibits an in-plane deformation owing to “scissor effects” as in $7d^{2+}$. With the formation of a new bond between the C_α and C_{ortho} atoms [1.6155(14) Å], one of the four fluorophenyl groups was transformed into a 5-methylene-1,3-hexadiene unit with a remarkable bond alternation. These geometrical features were well-reproduced by a DFT calculation of the structure of **5a** (Figure S2).^[16] The preferred formation of α,o -adduct **5a** over α,α -adduct **4a** can also be explained in terms of the estimated energy difference of 8.18 kcal mol⁻¹ in favor of **5a**. DFT calculations^[16] also indicate that with little or no influence from scissor effects, the α,α -adducts **3a** (X = H) and **2a** (X = H) are more stable than the corresponding α,o -adducts by 9.01 and 19.23 kcal mol⁻¹, respectively (Figure S2).

When substituents were attached next to the C_{ortho} carbon atoms, the α,o -coupling was suppressed. Upon reduction of 3,5-dimethylphenyl derivative $7c^{2+}-(TfO^-)_2$, hydrogenated compound **9c**^[19] rather than α,o -adduct **5c**, was obtained in 38 % yield over two steps (Scheme 4). In the presence of O_2 , peroxide **10c**^[23] was also obtained as a side product. Therefore, diradical 7^{2+} undergoes intermolecular reactions when the α,p -, α,α -, and α,o -coupling pathways are suppressed. X-ray analysis^[20] showed that the $C_\alpha-C_\alpha$ distances in **9c** and **10c** [d_3 = 3.258(4) and 3.316(2) Å, respectively] are close to the values determined for dication $7d^{2+}$, showing that the scissor effects place the two C_α carbon atoms of 7^{2+} far enough apart to accommodate two atoms (–H, H– or –O–O–) between them (Figure S3).

Upon reduction of 4-methoxyphenyl derivative $7d^{2+}-(BF_4^-)_2$ under argon atmosphere, α,o -adduct **5d**^[19] was obtained (40 % yield) whereas under oxygen atmosphere, peroxide **10d**^[19,20] was the major product (37 % yield). Its solid-state geometry [d_3 = 3.310(6) Å] was determined to be very similar to that of **10c** (Figure S3). This observation is in sharp contrast to the exclusive formation of α,o -adduct **5b** (80 % yield over two steps) under oxygen atmosphere upon reduction of 4-fluorophenyl derivative $7b^{2+}-(TfO^-)_2$. This difference in intermolecular reactivity between diradicals $7b^{2+}$ and $7d^{2+}$ can be rationalized by effects induced by the substituents at the 4-position of the aryl groups. In general, 4-substituted benzyl radicals are stabilized by a methoxy group ($\sigma_a^* = 0.034$)^[24] but destabilized by a fluorine substituent ($\sigma_a^* = -0.011$). Therefore, $7b^{2+}$ must be so short-lived that it undergoes rapid intramolecular α,o -coupling to give **5b** exclusively, whereas $7d^{2+}$ would have a longer lifetime to be involved in the intermolecular reaction with O_2 . Thus, for the high-yield formation of α,o -adduct **5**, the attachment of a radical-destabilizing group is preferred in the present system.

The α,o -adducts **5** obtained in this study are stable entities. No sign of decomposition or transformation into the aromatized isomer^[25] was observed when a toluene solution of **5b** was heated at reflux for four hours.^[27] Instead, we found that the unique reactivity of α,o -adducts **5** involved the cleavage of the newly formed $C_\alpha-C_{ortho}$ bond. According to a voltammetric analysis (Figure S4), **5d** undergoes facile two-electron oxidation owing to the presence of the electron-donating methoxy groups ($E^{ox} = +0.24$ V vs. Fc/Fc⁺ in CH_2Cl_2).^[28,29] The oxidation process is irreversible in the sense that the return peak was observed in the far cathodic region, which corresponds to the reduction of dication $7d^{2+}$ ($E^{red} = -0.30$ V). In fact, when **5d** was treated with two equivalents of (4-BrC₆H₄)₃N⁺SbCl₆⁻, $7d^{2+}-(SbCl_6^-)_2$ was isolated in 80 % yield. During the electrochemical transformation of **5d** into $7d^{2+}$, a continuous change in the UV/Vis spectrum with several isosbestic points was observed accompanied by a vivid color change from yellow to deep red (Figure S5).

In summary, we have succeeded in generating the first α,o -adduct by combining two trityl radicals into the 1*H*-cyclobuta[de]naphthalene skeleton, which exhibited pronounced scissor effects as demonstrated by a series of X-ray analyses. Future studies should consider not only their structural novelty, but also their properties, such as chromism.

Keywords: dimerization · radicals · steric hindrance · strained molecules · X-ray diffraction

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- [20] Details of the crystallographic analyses are given in the Supporting Information. CCDC 1041335 (**5d**), 1041336 (**7d**²⁺-(BF₄⁻)₂), 1041337 (**10c**), 1041338 (**8d**²⁺-(BF₄⁻)₂-CH₂Cl₂), 1041339 (**10d**), and 1041340 (**9c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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