Radicals

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

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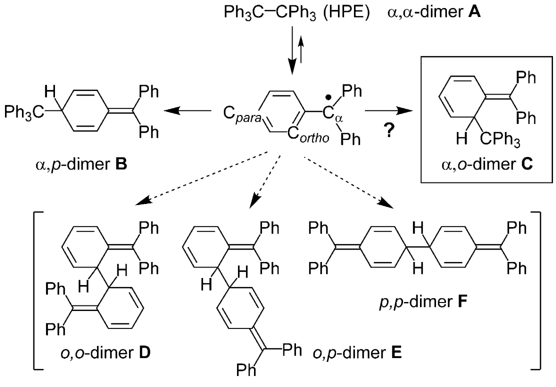
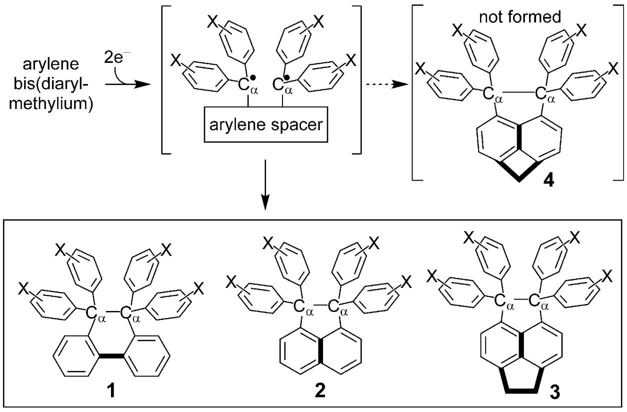
Dedicated to Prof. Yoshiro Yamashita

Abstract: *Upon reduction of a 1H-cyclobuta[de]naphthalene-4,5-diylbis(diarylmethylium) 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,o-adducts. The 5-diarylmethylene-6-triarylmethyl-1,3-cyclohexadiene unit in the α,o-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.*



Scheme 1. Dimerization modes of the trityl radical.



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

Hexaphenylethane (HPE, **A**) is a molecule with many riddles.[1] The trityl radical ($Ph_3C^\bullet$) dimerizes to form 3-diphenylmethylene-6-triphenylmethyl-1,4-cyclohexadiene (α,*p*-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,*p*-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] 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 *o*,*o*-, *o*,*p*-, 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,*o*-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 ($\Delta E = 6.63\ \mathrm{kcal\,mol^{-1}}$) as estimated by calculations employing the OPLS force field (Supporting Information, Figure S1),[14] there should be no reason for the absence of α,*o*-adducts, although such derivatives have never been described in the literature. As HPE derivatives (α,α-adducts) become accessible when the α,*p*-coupling is suppressed, the α,*o*-adducts should be generated

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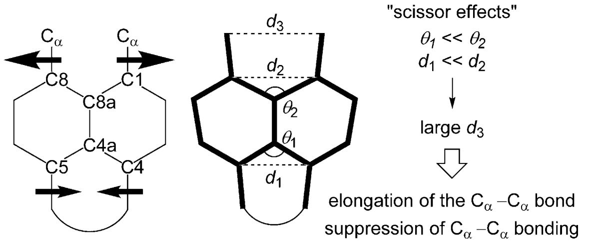
when the formation of the corresponding α,*p*- and α,α-adducts is prevented.

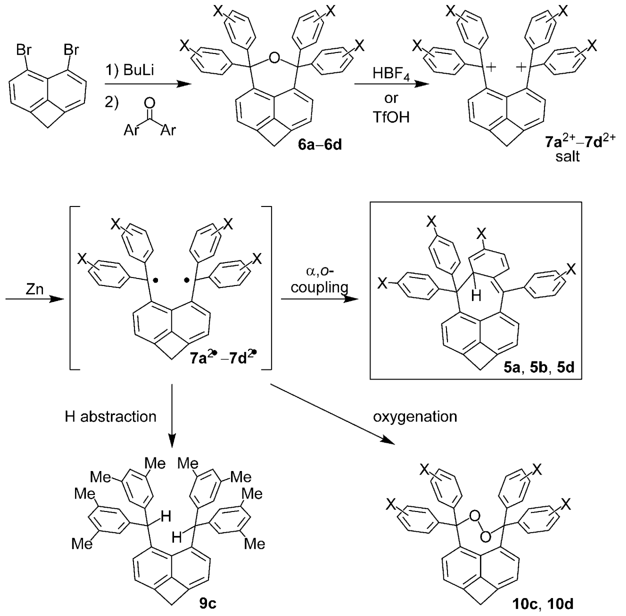
We planned to suppress the α,*p*-coupling by adopting the arylenediyl approach using a naphthalene-1,8-diyl skeleton as in **2**. The C_α and C_{ortho} carbon atoms of each radical unit are thus brought into close contact in addition to the two C_α atoms. "Scissor effects" through ring annulation at the opposite *peri* position of the naphthalene core were then considered (Scheme 3). The angle strain induced by annulation 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_α–C_α bonding because the interatomic distance d_3 is much greater in the precursor diradicals for **4** than in those for **3**.



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

In fact, we found that a series of compounds **3**, which display such scissor effects, have a longer C_α–C_α 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_α–C_α 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.

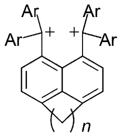
The reaction of 4,5-dibromo-1*H*-cyclobuta[*de*]naphthalene[18] with BuLi in diethyl ether followed by the addition of benzophenone gave pyran **6a**[19] (66 % yield) after acidic workup with trifluoroacetic acid (Scheme 4). The 4-fluoro-, 3,5-dimethyl-, and 4-methoxy-substituted derivatives (**6b**–**6d**)[19] were similarly obtained in yields of 59, 81, and 85 %, respectively. Upon treatment of pyrans **6a**–**6c** with TfOH in a mixture of $(CF_3)_2CHOH$ and CH_2Cl_2, the dications **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 HBF_4 in a mixture of trifluoroacetic anhydride and CH_2Cl_2, and **7d**$^{2+}$-$(BF_4^-)_2$[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 dications **7**$^{2+}$ along with several side products. **a**: X = H; **b**: X = 4-F; **c**: X = 3,5-Me$_2$; **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**$^{2+}$-$(BF_4^-)_2$. [c] In **8d**$^{2+}$-$(BF_4^-)_2$-CH_2Cl_2 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(diarylmethylium) salt **8d**$^{2+}$-$(BF_4^-)_2$,[20] the effects are much less pronounced in this five-membered-ring analogue. Consequently, the non-bonded C_α–C_α 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_α–C_α 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_α–C_α bond.[11,22] On the other hand, because of the C_α–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 $\mathbf{7}^{2+}$.

When a MeCN solution of $\mathbf{7a}^{2+}$-$(\mathrm{TfO}^-)_2$ 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). ^{1}H 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 $\mathbf{7b}^{2+}$-$(\mathrm{TfO}^-)_2$ gave yellow crystals of **5b**[19] (85 % yield over two steps); their structural identity was unambiguously confirmed by X-ray analysis (Figure 1).[20]

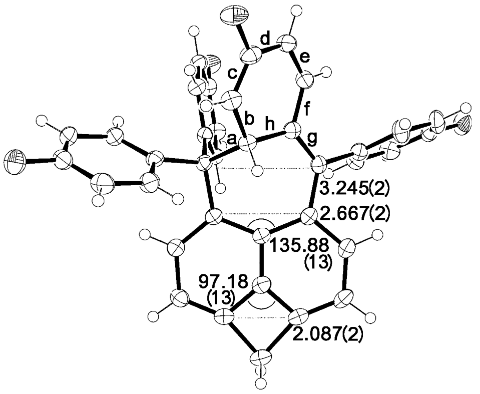


Figure 1. Molecular structure of α,*o*-adduct **5b** determined by X-ray analysis at 150 K. Selected bond lengths [Å]: a 1.6155(14), b 1.516(2), c 1.325(2), d 1.453(3), e 1.338(3), f 1.458(2), g 1.359(3), h 1.530(2).

The cyclobutanaphthalene unit also exhibits an in-plane deformation owing to "scissor effects" as in $\mathbf{7d}^{2+}$. 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 $\mathbf{7c}^{2+}$-$(\mathrm{TfO}^-)_2$, 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 $\mathbf{7}^{2\bullet}$ undergoes intermolecular reactions when the α,*p*-, α,α-, and α,*o*-coupling pathways are suppressed. X-ray analysis[20] showed that the C_α–C_α distances in **9c** and **10c** [$d_3 = 3.258(4)$ and 3.316(2) Å, respectively] are close to the values determined for dication $\mathbf{7d}^{2+}$, showing that the scissor effects place the two C_α carbon atoms of $\mathbf{7}^{2\bullet}$ far enough apart to accommodate two atoms (–H, H– or –O–O–) between them (Figure S3).

Upon reduction of 4-methoxyphenyl derivative $\mathbf{7d}^{2+}$-$(\mathrm{BF}_4^-)_2$ 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 $\mathbf{7b}^{2+}$-$(\mathrm{TfO}^-)_2$. This difference in intermolecular reactivity between diradicals $\mathbf{7b}^{2\bullet}$ and $\mathbf{7d}^{2\bullet}$ 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 ($\sigma_\alpha^\bullet = 0.034$)[24] but destabilized by a fluorine substituent ($\sigma_\alpha^\bullet = -0.011$). Therefore, $\mathbf{7b}^{2\bullet}$ must be so short-lived that it undergoes rapid intramolecular α,*o*-coupling to give **5b** exclusively, whereas $\mathbf{7d}^{2\bullet}$ 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_α–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 ($E^{\mathrm{ox}} = +0.24$ V vs. Fc/Fc$^+$ in $\mathrm{CH_2Cl_2}$).[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 $\mathbf{7d}^{2+}$ ($E^{\mathrm{red}} = -0.30$ V). In fact, when **5d** was treated with two equivalents of $(4\text{-}\mathrm{BrC_6H_4})_3\mathrm{N}^{+\bullet}\mathrm{SbCl_6}^-$, $\mathbf{7d}^{2+}$-$(\mathrm{SbCl_6}^-)_2$ was isolated in 80 % yield. During the electrochemical transformation of **5d** into $\mathbf{7d}^{2+}$, 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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[19] Experimental details and physical data of new compounds are given in the Supporting Information.

[20] Details of the crystallographic analyses are given in the Supporting Information. CCDC 1041335 (**5d**), 1041336 (**7d**$^{2+}$-(BF_4^-)$_2$), 1041337 (**10c**), 1041338 (**8d**$^{2+}$-(BF_4^-)$_2$-CH_2Cl_2), 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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[29] As shown in Figure S4, the voltammograms of **5a** ($E^{ox} = +0.32$ V vs. Fc/Fc$^+$) and **5b** (+0.43 V) resemble that of **5d** in shape, indicating that the C_α–C_{ortho} bond in **5a** and **5b** would also be cleaved upon oxidation.

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