Chemistry
A European
Journal

Chemistry Europe
European Chemical Societies Publishing

Accepted Article

Title: Thermodynamically Stable o-Quinodimethane: Synthesis, Structure, and Reactivity

Authors: Toshiyuki Hamura, Kazuhiko Adachi, Shunsuke Hirose, Yasuyuki Ueda, and Hidehiro Uekusa

To be cited as: *Chem. Eur. J.* 10.1002/chem.202004510

Link to VoR: https://doi.org/10.1002/chem.202004510

WILEY-VCH

10.1002/chem.202004510

WILEY-VCH

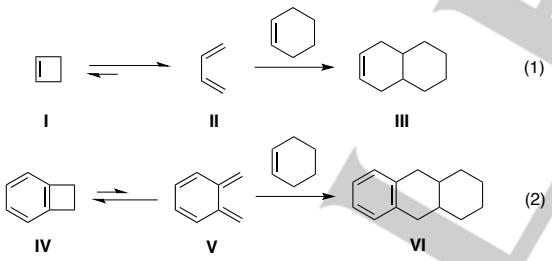
Thermodynamically Stable *o*-Quinodimethane: Synthesis, Structure, and Reactivity

Kazuhiko Adachi,[a] Shunsuke Hirose,[a] Yasuyuki Ueda,[a] Hidehiro Uekusa,[b] and Toshiyuki Hamura*[a]

Dedication ((optional))

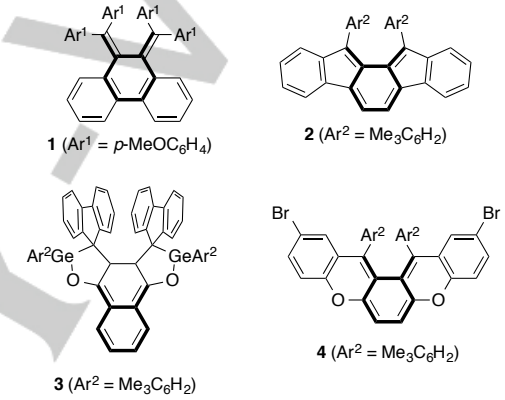
Abstract: Thermal isomerization of cyclobutaphenanthrene to *o*-quinodimethane was investigated. Sterically congested substituents or electron-donating substituents on the four-membered ring promoted the ring-opening, affording *o*-quinodimethane in a relatively stable form. Isolation of the newly prepared *o*-quinodimethane allowed its structural elucidation and investigation of its potential reactivities. Dual [4+2] cycloaddition of an aryne and *o*-quinodimethane afforded tetrabenzopentacene, demonstrating the synthetic application of the isolated compound.

Thermal isomerization of cyclobutene to 1,3-diene (Scheme 1) is one of the most fundamental and useful reactions, since the ring-opened isomer can further react with dienophiles to give polycyclic compounds, which are key intermediates in the syntheses of various natural and synthetic products.[1] The first step (**I** → **II**) in this pericyclic cascade reaction is exothermic owing to release of the inherent ring strain in the four-membered ring (Eq. 1). An opposite behavior is observed for the case of benzocyclobutene **IV**, the benzo-analogue of cyclobutene **I**, due to the loss of aromaticity of the benzene ring in **IV** (Eq. 2). Consequently, *o*-quinodimethane **V**, the ring-opened isomer of **IV**, is obtained only as a transient intermediate, thereby limiting the potential utility of this structurally attractive molecule.[2,3]



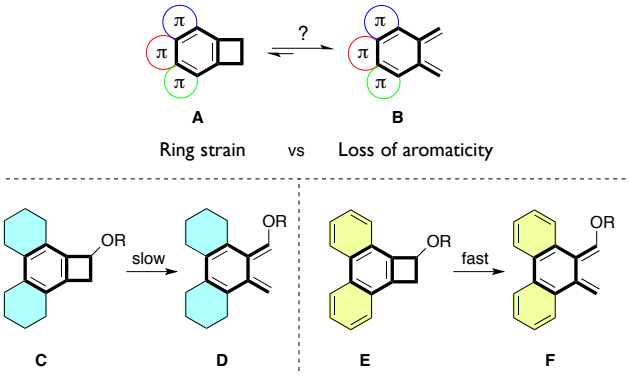
Scheme 1. Pericyclic cascade reaction of cyclobutene **I** and benzocyclobutene **IV**.

Thermally stable *o*-quinodimethanes (e.g., **1**–**4**) have been synthesized previously, and several unique properties including biradical characters, small band gaps, and excellent electrochemical behaviors have been observed (Scheme 2).[4] However, steric protection by the sterically congested substituents and/or fused ring in the butadiene moiety of these compounds prevents their isomerization into the four-membered ring. Due to this, their synthetic use as a quinoidal building block is virtually difficult. Moreover, the steric protection renders these quinodimethanes kinetically stable.



Scheme 2. Representative examples of isolable *o*-quinodimethanes.

Considering this, we adopted an approach to prepare *isolable* *o*-quinodimethanes that were not kinetically stabilized (Scheme 3). To access the ring-opened structure, we introduced extra aromatic rings onto the parent structure **IV** to reduce the destabilization caused by the ring opening (**A** → **B**). In this π-extended system, if the energy loss due to dearomatization of the benzene ring in **A** is smaller than the ring strain of the four-membered ring, the ring-opened isomer **B** would become energetically more favorable than the ring-closed form **A**, thus, producing thermodynamically stable quinodimethane **B**.[5]



Scheme 3. Synthetic strategy to access to isolable *o*-quinodimethane.

[a] Dr. K. Adachi, Mr. S. Hirose, Dr. Y. Ueda, Prof. Dr. T. Hamura
Department of Applied Chemistry for Environment, Kwansei Gakuin University, 2-1 Gakuen, Sanda 669-1337, Japan
E-mail: thamura@kwansei.ac.jp
[b] Prof. Dr. H. Uekusa
Department of Chemistry, School of Science, Tokyo Institute of Technology, Ookayama 2, Meguro-ku, Tokyo 152-8551, Japan

Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate))

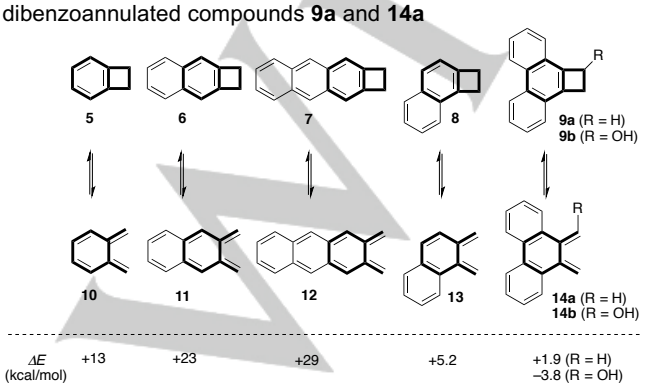
The basis for this strategy lies in our related work for the synthesis of π-extended triphenylenes by the successive cycloaddition of tricyclobutabenzene.[6] Specifically, cyclobutaphenantrene **E**, obtained by double cycloaddition and acid-promoted aromatization of tricyclobutabenzene, had higher propensity for ring-opening than the non-aromatic cyclobutabenzene **C** and gave the Diels–Alder cycloadduct at lower temperatures by the facile generation of quinodimethane **F**.

We thus focused on the syntheses of cyclobutaarenes containing extra aromatic rings on the parent benzocyclobutene. Although the interconversion between cyclobutabenzene **IV** and *o*-quinodimethane **V** has been thoroughly studied, the poly-aromatic analogues with various potential functionalities have remained unexplored, presumably due to the poor availability.

Herein, we demonstrate that cyclobutaphenanthrene **E**, efficiently prepared by the (2+2) cycloaddition of an aryne and ketene silyl acetal (KSA), underwent thermal isomerization to afford the corresponding ring-opened isomer **F** as a relatively stable product, provided the hydroxy group on the four-membered ring in **E** is protected using a suitable substituent.[7,8] Moreover, structure of the isolated *o*-quinodimethane was characterized by X-ray crystallographic analysis, and its reactivity was investigated through the trapping reaction with a transiently generated aryne to afford the structurally attractive tetrabenzopentacene.

We initially performed density functional theory calculations to determine the thermodynamic preference between cyclobutaarene and the corresponding ring-opened isomer and to estimate the effect of π-extension on the ring-opening (Scheme 4). Energy gap between the two isomers of the parent system (ΔE_{10-5}) was +13 kcal/mol. When an additional benzene ring was introduced at the *para* position of the parent benzocyclobutene **5**, energy gap between the cyclic and ring-opened product increased significantly; that is, energy of quinodimethane **11** was much higher than that of cyclobutanaphthalene **6** (ΔE_{11-6} = +23 kcal/mol). Further addition of a benzene ring at the *para* position resulted in an even larger energy gap (ΔE_{12-7} = +29 kcal/mol). This trend can be explained by the increased quinoidal character owing to the fusion of the benzene ring at the *para* position.

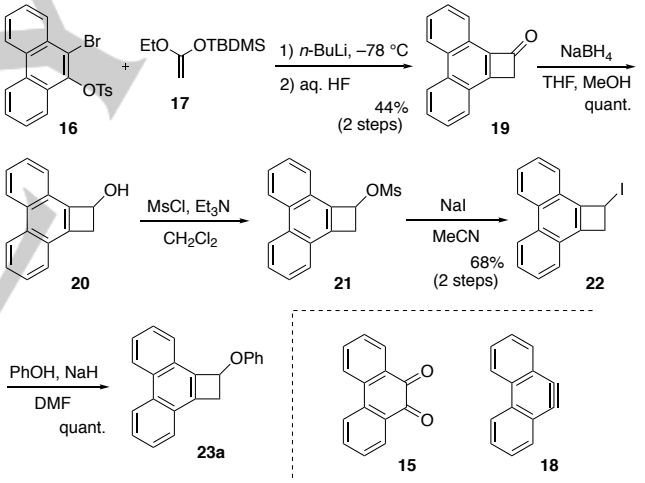
In contrast, an opposite trend was observed for the *meta*-fused cyclobutaarenes. The energy gap between cyclobutanaphthalene **8** and its ring-opened isomer **13** was 5.2 kcal/mol, and the energy gap further decreased for dibenzoannulated compounds **9a** and **14a**



Scheme 4. Thermodynamic preference ($\Delta E_{ring\text{-}opened-ring\text{-}closed}$) between cyclobutaarenes and their ring-opened isomers calculated at the B3LYP-D3/6-311G(d,p) level with Grimme's dispersion correction.

($\Delta E_{14a-13a}$ = +1.9 kcal/mol). This indicates that among mono- and di-annulated cyclobutabenzenes **5**–**9**, phenanthrene-based condensations most efficiently promote the formation of *o*-quinodimethane. In addition to this π-extension, introduction of the hydroxy group on the four-membered ring strongly facilitates the ring opening, rendering *o*-quinodimethane **14b** a thermodynamically stable product ($\Delta E_{14b-13b}$ = –3.8 kcal/mol).[9]

Based on these calculations, cyclobutaphenanthrenes **23** bearing an electron donating aryloxy group on the four-membered ring were prepared as a precursor of *o*-quinodimethane (Scheme 5). Reaction of bromo tosylate **16**, which is easily accessible from phenanthrene-9,10-dione **15**,[10] with *n*-BuLi in the presence of KSA **17** gave the (2+2) cycloadduct (structure not shown) via the formation of aryne **18**;[11] acid-promoted hydrolysis of the cycloadduct afforded cyclobutenone **19**. Further transformations, including the reduction of the carbonyl group in **19** and the S_N2 reaction of iodide **22** with sodium phenoxide gave cyclobutaphenanthrene **23a**. Other aryl ethers, **23b**–**23k** (Table 1), could also be accessed through the S_N2 reaction of iodide **22** with ArONa.



Scheme 5. Synthesis of cyclobutaphenanthrene via (2+2) cycloaddition of aryne and KSA.

The thermal reaction of cyclobutaphenanthrene **23a** was monitored by VT NMR spectroscopy (toluene-d_8, 90 °C), and the spectra are shown in Figure 1. Heating **23a** at 90 °C afforded the ring-opened product **24a**, as evident from the appearance of two sets of doublets and one singlet corresponding to **24a** (spectrum (b)). After 1 h, the interconversion reached equilibrium, and the **23a**/**24a** product ratio was 76:24 (spectrum (c)).[12] This indicates that the ring-opened form was thermodynamically less stable than the ring-closed form. After removing the solvent, the reaction mixture was separated by preparative TLC to give quinodimethane **24a** in 29% yield as a single

10.1002/chem.202004510

isomer.[13] Quinodimethane **24a** was determined to be an *E* isomer based on the X-ray analysis of a related compound (vide infra). Importantly, product **24a** could be stored in a refrigerator for several months.[14]

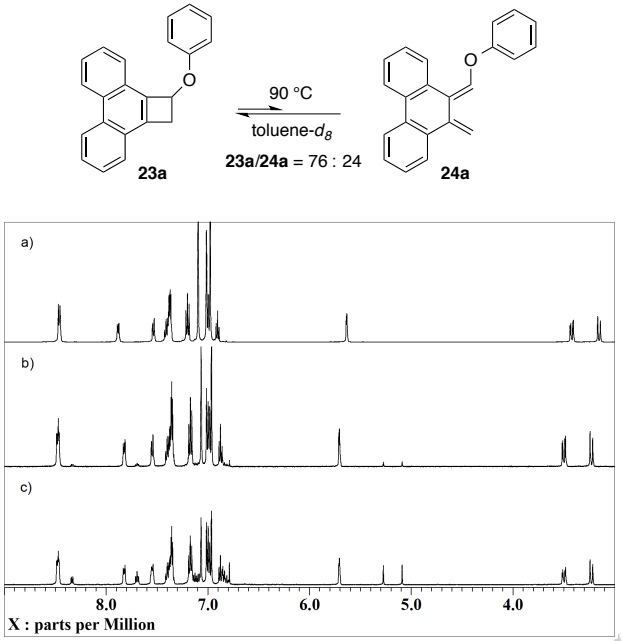
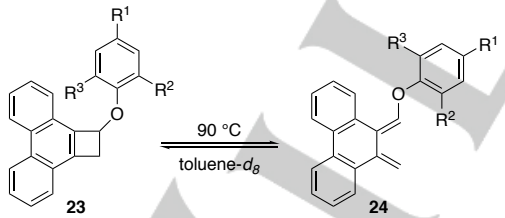


Figure 1. Thermal isomerization of **23a** monitored by VT ^{1}H NMR spectroscopy (500 MHz, [D_8]toluene, 90 °C). a) **23a** (RT), b) reaction mixture after 5 min (90 °C), c) reaction mixture after 1 h (90 °C).

Aryl ethers **23b**–**23k** with various substitution patterns were also heated under similar conditions, and the ratios of the ring closed form **23** and ring opened form **24** were determined (Table 1).

Table 1. Thermal isomerization of cyclobutaphenanthrenes **23** to *o*-quinodimethanes **24**.



Entry	Cyclobutene	R^1	R^2	R^3	Molar ratio **23** : **24**
1	**23b**	Me	H	H	66 : 34
2	**23c**	OMe	H	H	63 : 37
3	**23d**	NMe_2	H	H	52 : 48
4	**23e**	F	H	H	82 : 18
5	**23f**	Cl	H	H	81 : 19
6	**23g**	CHO	H	H	89 : 11
7	**23h**	NO_2	H	H	92 : 8
8	**23i**	H	Me	H	65 : 35
9	**23j**	H	Me	Me	15 : 85
10	**23k**	H	Ph	Ph	33 : 67

Introduction of an electron-donating group at the *para* position increased the proportion of the ring-opened form relative to the proportion of **23a** (entries 1–3). Indeed, the ratio of aryl ether **23d**, bearing a dimethylamino group, to *o*-quinodimethane **24d** after isomerization was 52:48. In sharp contrast, introduction of electron-withdrawing groups at the *para* position decreased the proportion of the ring-opened form with increasing electron-withdrawing ability of the substituents (entries 4–7). For substrate **23h** having a nitro group, the corresponding ring-opened isomer **24h** was obtained only in 8% yield (NMR yield).[15]

Moreover, it is interesting to note that the ring-opened isomer was produced predominantly when substrates **23j** and **23k** bearing sterically congested aryloxy group on the four-membered ring were heated (entries 9 and 10). Gratifyingly, *o*-quinodimethane **24k** having a terphenyloxy group could be purified by preparative TLC, and slow crystallization of **24k** gave single crystals suitable for X-ray analysis.

Figure 2 shows the X-ray structure of **24k**.[16] The twisted nature of **24k** in the solid state was a striking feature; the twist angle of the biphenyl backbone was 17.2°, and the torsion angle of the two exocyclic double bonds was 41.7°. The C–C bonds around the central six-membered ring exhibited bond length alternation (C1–C2 = 1.335 Å, C2–C3 = 1.478 Å, C3–C4 = 1.408 Å, C4–C5 = 1.480 Å, C5–C6 = 1.412 Å, C6–C7 = 1.476 Å, C7–C8 = 1.342 Å, C7–C2 = 1.484 Å), which is similar to that observed in the structure of *o*-quinodimethane **1**.

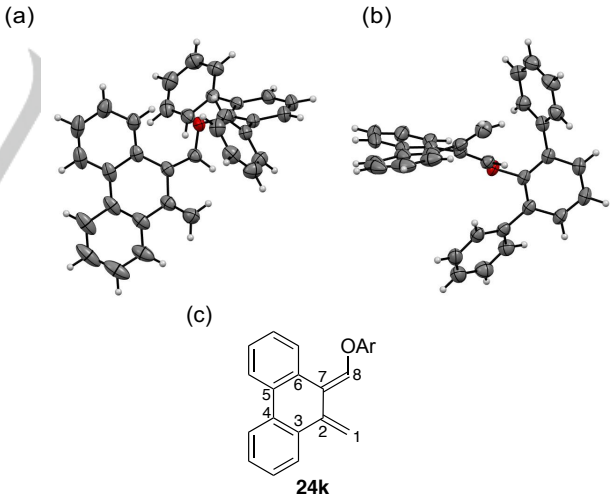
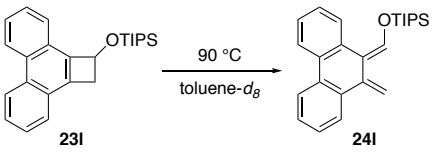


Figure 2. X-ray structure of *o*-quinodimethane **24k**. a) top view, b) side view, c) the number of carbon atoms in **24k**.

Further investigation of the thermal isomerization of cyclobutaphenanthrene revealed that the siloxy group on the four-membered ring contributed substantially to promote the ring opening, affording *o*-quinodimethane as an almost exclusive product. The VT-NMR spectrum of silyl ether **23l** clearly shows that the peaks of starting compound **23l** gradually disappeared upon heating in toluene-d_8 at 90 °C (spectrum (b)

in Figure 3). After 20 min, the starting compound was almost completely converted to *o*-quinodimethane **24l** (spectrum (c)).[17] The electron-donating ability of the substituent on the four-membered ring is an important factor in controlling the ring-opening step. Thus, in addition to facilitating the ring opening, which is known as torquoselectivity,[9] the higher electron donating ability of the siloxy group compared to the aryloxy group[18] may stabilize the quinodimethane.[19]



23l **24l**

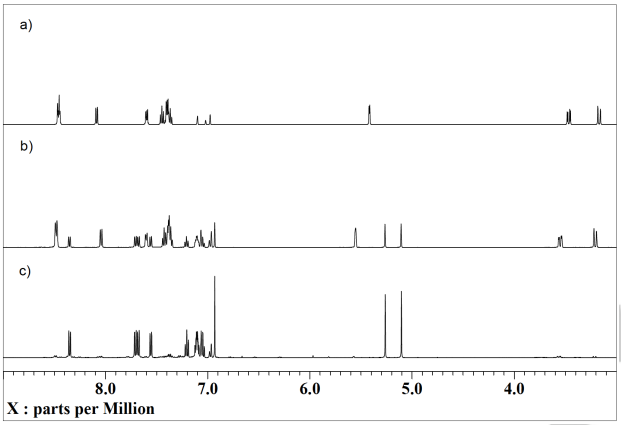
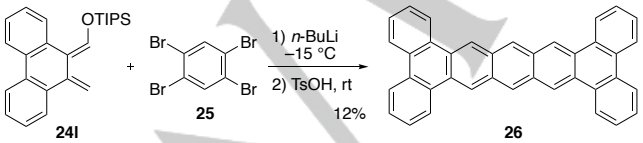


Figure 3. Thermal reaction of **23l** monitored by ^{1}H NMR spectroscopy (500 MHz, toluene-d_8, 90 °C). a) **23l** (RT), b) reaction mixture after 5 min (90 °C), c) reaction mixture after 20 min (90 °C).

Interestingly, the discovery of a method to prepare isolable *o*-quinodimethane provided a new opportunity for the reaction of this compound with another reactive intermediate. Such reactions are otherwise difficult, because *o*-quinodimethane is usually obtained as a transient intermediate. Tetrabromobenzene (**25**) served as a bis-benzyne equivalent,[20] and its treatment with *n*-BuLi in the presence of quinodimethane **24l** resulted in dual [4+2] cycloaddition to give tetrabenzopentacene **26**, after the acid-promoted aromatization of the dual cycloadduct (Scheme 6).[21–24]



24l **25** **26**

Scheme 6. Dual [4+2] cycloaddition of aryne and *o*-quinodimethane **24l** for the synthesis of tetrabenzopentacene **26**.

In summary, we demonstrated that *o*-quinodimethane, a thermodynamically stable π-extended diene system, could be prepared via the thermal ring-opening of cyclobutaphenanthrene by introducing an electron-donating substituent on the four-membered ring. The *o*-quinodimethanes obtained through this strategy can be used as a reactive platform to access novel polycyclic aromatic compounds with interesting properties. Further synthetic applications, including the derivatization to more π-extended *o*-quinodimethanes with various substitution patterns, are being investigated in our laboratory.

Acknowledgements

This work was supported by JSPS KAKENHI Grant Number JP15H05840 in Middle Molecular Strategy and JST ACT-C Grant Number JPMJCR12YY, Japan.

Keywords: • quinodimethanes • cyclobutaarenes • cycloaddition • aryne • polycyclic aromatic hydrocarbon

[1] a) N. Gauvry, C. Lescop, F. Huet, *Eur. J. Org. Chem.* **2006**, 5207–5218; b) M. Murakami, T. Matsuda, In *Comprehensive Organic Synthesis II*, P. Knochel, G. A. Molander, Ed., Elsevier, Amsterdam, 2014, vol. 5, pp. 732–782; c) N. S. Sheikh, *Org. Biomol. Chem.* **2015**, *13*, 10774–10796; d) A. Misale, S. Niyomchon, N. Maulide, *Acc. Chem. Res.* **2016**, *49*, 2444–2458.

[2] For reviews of quinodimethanes, see: a) J. L. Segura, N. Martin, *Chem. Rev*. **1999**, *99*, 3199−3246; b) G. Mehta, S. Kotha, *Tetrahedron* **2001**, *57*, 625–659; c) A. K. Sadana, R. K. Saini, W. E. Billups, *Chem. Rev.* **2003**, *103*, 1539–1602; d) H. Yoshida, J. Ohshita, A. Kunai, *Bull. Chem. Soc. Jpn*. **2010**, *83*, 199−219; e) B. Yang, S. Gao, *Chem. Soc. Rev*. **2018**, *47*, 7926–7953.

[3] For selective synthetic examples of quinodimethanes, see: a) J. J. Fitzgerald, N. E. Drysdale, R. A. Olofson, *J. Org. Chem.* **1992**, *57*, 7122–7126; b) J. G. Allen, M. F. Hentemann, S. J. Danishefsky, *J. Am. Chem. Soc.* **2000**, *122*, 571–575; c) J. Barluenga, P. García-García, M. A. Fernández-Rodríguez, E. Aguilar, I. Merino, *Angew. Chem. Int. Ed.* **2005**, *44*, 5875–5878; d) T. Suzuki, T. Hamura, K. Suzuki, *Angew. Chem. Int. Ed.* **2008**, *47*, 2248–2252; e) K. Mori, K. Ohmori, K. Suzuki, *Angew. Chem. Int. Ed.* **2009**, *48*, 5633–5637.

[4] a) S. Iwashita, E. Ohta, H. Higuchi, H. Kawai, K. Fujiwara, K. Ono, M. Takenaka, T. Suzuki, *Chem. Commun*. **2004**, 2076−2077; b) T. Suzuki, Y. Sakano, T. Iwai, S. Iwashita, Y. Miura, R. Katoono, H. Kawai, K. Fujiwara, Y. Tsuji, T. Fukushima, *Chem. Eur. J*. **2013**, *19*, 117−123; c) A. Shimizu, Y. Tobe, *Angew. Chem., Int. Ed*. **2011**, *50*, 6906−6910; d) H. Miyoshi, S. Nobusue, A. Shimizu, I. Hisaki, M. Miyata, Y. Tobe, *Chem. Sci*. **2014**, *5*, 163–168; e) C. Sato, S. Suzuki, M. Kozaki, K. Okada, *Org. Lett*. **2016**, *18*, 1052–1055.

[5] Based on the Clar's aromatic sextet, we can also say that extra benzoannulation can make the ring-opened form more favorable than the parent system (**IV**→**V**) in view the difference of number of Clar's aromatic sextet before and after the isomerization.

[6] a) T. Hamura, Y. busuki, H. Uekusa, T. Matsumoto, K. Suzuki, *J. Am. Chem. Soc*. **2006**, *128*, 3534–3535; b) T. Hamura, Y. Ibusuki, H. Uekusa, T. Matsumoto, J. S. Siegel, K. K. Baldridge, K. Suzuki, *J. Am. Chem. Soc*. **2006**, *128*, 10032–10033; c) S. Shinozaki, T. Hamura, Y. Ibusuki, K. Fujii, H. Uekusa, K. Suzuki, *Angew. Chem., Int. Ed*. **2010**, *49*, 3026−3029. a) S. Shinozaki, T. Hamura, Y. Ibusuki, K. Fujii, H. Uekusa, K. Suzuki, *Angew. Chem. Int. Ed.* **2010**, *49*, 3026–3029; b) H. Tozawa, T. Kakuda, K. Adachi, T. Hamura, *Org. Lett.* **2017**, *19*, 4118–4121.

[7] Some parts of this work were presented at the annual meeting of the Chemical Society of Japan during 2012–2019, see: a) S. Hirose, T.

Hamura, *Abstracts of Papers*, 92nd Annual Meeting of The Chemical Society of Japan, The Chemical Society of Japan, Tokyo, **2012**, 3M1–40; b) K. Adachi, S. Hirose, T. Hamura, *Abstracts of Papers*, 96th Annual Meeting of The Chemical Society of Japan, The Chemical Society of Japan, Tokyo, **2016**, 1H4–08; c) K. Adachi, T. Hamura, *Abstracts of Papers*, 99th Annual Meeting of The Chemical Society of Japan, The Chemical Society of Japan, Tokyo, **2019**, 2I3–47.

[8] Recently, an efficient synthetic route to benzo-annulated quinodimethanes was developed via intramolecular reductive cyclization of a diyne with a low-valent zirconocene reagent. In these cases, the products, isolated, were isomerized to ring-closed cyclobutaarenes upon heating, see: G. R. Kiel, M. S. Ziegler, T. D. Tilley, *Angew. Chem. Int. Ed.* **2017**, *56*, 4839–4844.

[9] a) W. R. Dolbier, H. Koroniak, K. N. Houk, C. Sheu, *Acc. Chem. Res.* **1996**, *29*, 471–477; b) W. KirMSe, N. G. Rondan, K. N. Houk, *J. Am. Chem. Soc.* **1984**, *106*, 7989; c) S. Niwayama, E. A. Kallel, C. Sheu, K. N. Houk, *J. Org. Chem.* **1996**, *61*, 2517; d) S. Niwayama, E. A. Kallel, D. C. Spellmeyer, C. Sheu, K. N. Houk, *J. Org. Chem.* **1996**, *61*, 2813.

[10] For details, see supporting information.

[11] For selected reviews on arynes: a) R. W. Hoffmann, *Dehydrobenzene and Cycloalkynes*, Academic, New York, 1967; b) S. V. Kessar, In *Comprehensive Organic Synthesis*; Trost, B. M. Ed., Pergamon: Oxford, U. K., 1991, Vol. 4, pp. 483–515; c) H. Pellissier, M. Santelli, *Tetrahedron*, **2003**, *59*, 701–730; d) H. H. Wenk, M. Winkler, W. Sander, *Angew. Chem. Int. Ed*. **2003**, *42*, 502–528; e) H. Yoshida, K. Takaki, *Synlett*, **2012**, *23*, 1725–1732; f) A. Bhunia, S. R. Yetra, A. T. Biju, *Chem. Soc. Rev*. **2012**, *41*, 3140–3152; g) A. V. Dubrovskiy, N. A. Markina, R. C. Larock, *Org. Biomol. Chem*. **2013**, *11*, 191–218.

[12] Quinodimethane **24a** thus formed was gradually decomposed upon further heating at the same temperature.

[13] Quinodimethane **24a** was prone to hydrolysis, owing to the lability of the enol ether moiety.

[14] Retro-cyclization of the isolated o-quinodimethane **24a** to cyclobutene **23a** was observed by heating **24a** in toluene-d_8 at 90 °C, although the decomposed products were also detected.

[15] Due to the instability of o-quinodimethanes **24f** and **24h** and the low yields of the reactions, the ^{13}C NMR spectra could not be obtained.

[16] $C_{34}H_{24}O$, MW = 448.53, 0.20 x 0.10 x 0.10 mm, Monoclinic, space group $P2_1/n$, Z = 16, T = 173(2) K, a = 23.0307(4) Å, b = 17.9972(3) Å, c = 23.4198(4) Å, β = 92.5300(10)°, V = 9697.8(3) Å^3, λ(CuKα) = 1.54186 Å, μ = 0.557 mm^{-1}. Intensity data were collected on a Rigaku RAXIS-RAPID IP. The structure was solved by direct methods (SHELXS97) and refined by the full-matrix least-squares on F^2 (SHELXL97). A total of 110653 reflections were measured, and 17435 were independent. Final R_1 = 0.0457, wR_2 = 0.1264 (14799 refs; $I > 2\sigma(I)$), and GOF = 1.065 (for all data, R_1 = 0.0519, wR_2 = 0.1308).

[17] Although clean formation of **24l** was evident from the ^{1}H NMR analysis, it was highly prone to hydrolysis during chromatography on silica-gel, affording **24l** in 29% isolated yield. Due to this, the unpurified product was used for further functionalization.

[18] a) H. Mayr, B. Kempf, A. R. Ofial, *Acc. Chem. Res.* **2003**, *36*, 66–77; b) N. Streidl, B. Denegri, O. Kronja, H. Mayr, *Acc. Chem. Res.* **2010**, *43*, 1537–1549; c) H. Mayr, A. R. Ofial, *Acc. Chem. Res.* **2016**, *49*, 952–965; d) H. Mayr, A. R. Ofial, *Pure Appl. Chem.* **2017**, *89*, 729–744.

[19] Origin of the ring-opening selectivity depending on the substituent on the four-membered ring is thoroughly investigated, which will be described in the forthcoming paper.

[20] Tetrabromobenzene (**25**) can serve as a 1,4-benzdiyne equivalent. For pioneering studies by Hart on the generation and trapping of 1,4-benzdiyne equivalents, see: a) H. Hart, D. Ok, *J. Org. Chem.* **1986**, *51*, 979–986. (b) H. Hart, C.-Y. Lai, G. Nwokogu, S. Shamouilian, A. Teuerstein, C. Zlotogorski, *J. Am. Chem. Soc.* **1980**, *102*, 6649–6651. Other examples, see: c) Y.-L. Chen, J.-Q. Sun, X. Wei, W.-W. Wong, A. W. M. Lee, *J. Org. Chem.* **2004**, *69*, 7190–7197; d) G. E. Morton, A. G. M. Barrett, *J. Org. Chem.* **2005**, *70*, 3525–3529; e) I. I. Schuster, L. Cracium, D. M. Ho, R. A. Pascal, Jr., *Tetrahedron,* **2002**, *58*, 8875–8882; f) H. M. Duong, M. Bendikov, D. Steiger, Q. Zhang, G. Sonmez, J. Yamada, F. Wudl, *Org. Lett*. **2003**, *5*, 4433–4436.

[21] The dual cycloadduct consisted of regio- and stereoisomers with respect to the siloxy group, which were directly converted to tetrabenzopentacene **26**.

[22] Although **26** is obtained in moderate yield, the formation of four C–C bonds in a single process through dual-cycloaddition and the rapid access to a highly condensed structure show the potential utility of this reaction.

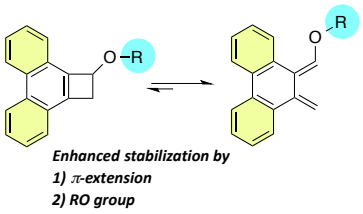
[23] Due to the low solubility of tetrabenzopentacene **26** in common organic solvents, the ^{13}C NMR spectra could not be obtained.

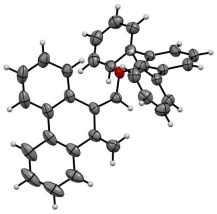
[24] For the previously reported synthesis of tetrabenzopentacene **26**, see a) E. Clar, W. Kely, W. G. Niven, *J. Chem. Soc.* **1956**, 1833–1836; b) K. G. Upul, R. Kumarasinghe, F. R. Fronczek, H. U. Valle, A. Sygula, *Org. Lett.* **2016**, *18*, 3054–3057.

10.1002/chem.202004510

WILEY-VCH

COMMUNICATION





*Kazuhiko Adachi, Shunsuke Hirose, Yasuyuki Ueda, Hidehiro Uekusa, and Toshiyuki Hamura**

Page No. – Page No.

Thermodynamically Stable *o*-Quinodimethane: Synthesis, Structure, and Reactivity

Isolable *o*-quiondimethanes were prepared by thermal ring-opening of cyclobutaphenanthrenes. In addition to benzo-annulation on parent benzocyclobutene, sterically congested aryloxy or siloxy group on the four-membered ring promoted the ring-opening, affording a thermodynamically stable π-extended *o*-quinodimethane.