

First stable 7,7,8,8-tetraaryl-*o*-quinodimethane: isolation, X-ray structure, electrochromic response of 9,10-bis(dianisylmethylene)-9,10-dihydrophenanthrene†

Shinichi Iwashita,^a Eisuke Ohta,^a Hiroki Higuchi,^a Hidetoshi Kawai,^a Kenshu Fujiwara,^a Kazunori Ono,^b Masami Takenaka^b and Takanori Suzuki^{*a}

^a Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan.

E-mail: tak@sci.hokudai.ac.jp; Fax: +81-11-706-2714; Tel: +81-11-706-2714

^b Asahi Kasei Electronics Co., Shioya, Hichiya, Hyuga 883-0062, Japan

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Oxidative cyclization of 2,2'-bis(dianisylethenyl)biphenyl yielded the dicationic salt of phenanthrene-9,10-diylbis(dianisylmethylum), which in turn afforded the severely congested title molecule as the first stable tetraaryl-*o*-quinodimethane derivative upon reduction.

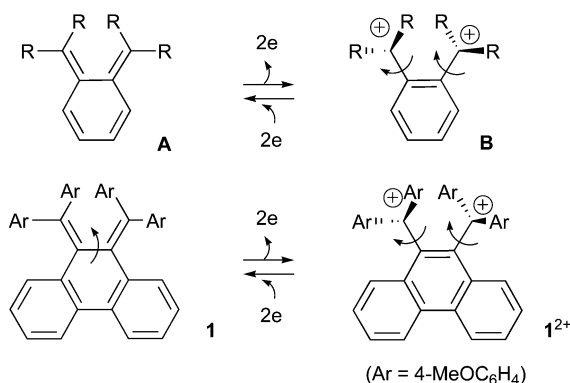
o-Quinodimethane (oQDM; A, R = H) has been known as a short-lived reactive hydrocarbon and used as a versatile building block in synthetic chemistry.¹ From the viewpoint of multistage redox systems,² this skeleton serves as an attractive scaffold to construct a Wurster-type redox pair by attaching the proper end groups at the termini of the *exo*-methylene carbons (A, R = charge-stabilizing group).³ Outstanding features of oQDM-based redox systems will be drastic geometric changes upon electron transfer when the end groups are bulky enough to adopt nonplanar structures. Thus, the two *exo*-methylenes in the neutral molecule will form a large torsion angle whereas the *o*-xylylene unit will become planar in the doubly charged ion to which the charged end groups being attached nearly perpendicularly as in B (Scheme 1). By considering the fact that such structural changes are favorable to constructing molecular response systems in terms of reversibility and bistability,^{4,5} we have designed a novel electron donor 1 with four anisyl (4-MeOC₆H₄) groups as cation-stabilizing end groups. Two extra benzene rings are annelated to the oQDM skeleton in order to prevent 1 from diminishing by cyclization to the benzocyclobutene-type or triaryldihydroanthracene-type isomers.^{6,7} Here we report the successful preparation of 1 as a first isolable member of tetraaryl-oQDMs along with its severely deformed structure determined by low-temperature X-ray analysis. A noteworthy feature is that 1 and 9,10-phenanthrenediyl dication 1²⁺ constitute a reversible redox pair exhibiting an electrochromic response with vivid change in color.

The reaction of 2,2'-bitolyl with BuLi in the presence of

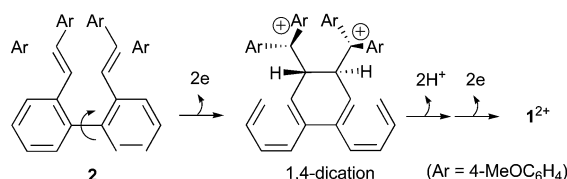
TMEDA gave 2,2'-bis(lithiomethyl)biphenyl,⁸ which was then treated with 4,4'-dimethoxybenzophenone in THF. The resulting diol was treated with a catalytic amount of TsOH in refluxing benzene to give diolefin 2⁹ in 50% yield over two steps. According to the X-ray analysis,¹⁰ 2 adopts a pseudo-C₂ symmetry with a twisting angle of 82.9° around the biphenyl axis (Figure S1†). Although the two benzyldiene carbons are separated by 3.85 Å in this solid-state structure, the oxidative cyclization^{11,12} proceeded smoothly as follows. Upon treatment of diolefin 2 with 4 equivalents of NOBF₄ in CH₂Cl₂, the dark purple powder of dicationic salt 1²⁺(BF₄[−])₂ was obtained in 92% yield. When a smaller amount of oxidant was used, the same salt was obtained accompanied by recovery of the starting material 2, suggesting that the 1,4-dication formed by 2e oxidation of 2 underwent facile deprotonation to 1 which is more easily oxidized under the reaction conditions to 1²⁺ (Scheme 2).^{11,13}

Upon treatment of 1²⁺(BF₄[−])₂ with excess Zn powder in DME, the deep purple color disappeared rapidly, and oQDM 1⁹ was isolated as surprisingly stable yellow cubes in 92% yield after recrystallization from CH₂Cl₂-hexane. Its thermal stability was demonstrated by quantitative recovery after refluxing for 24 h in toluene with no signs of electrocyclization to its isomers.¹⁴ In order to determine the detailed structural features of the first isolable derivative of 7,7,8,8-tetraaryl-oQDM, its X-ray analysis was conducted at −150 °C (Fig. 1).¹⁰ The most striking feature is the large torsion angle of 63.4° for the Ar₂C=C=CAr₂ unit although the twisting angle of the biphenyl skeleton is only 19.3°.¹⁵ Such deformation is surely induced to avoid the anomalous proximity of two inner anisyl groups, which are still close enough for π-π interaction: they are overlapped in a face-to-face manner with an interplanar distance of 3.35 Å and a dihedral angle of 13.2°. The closest contact between the aromatic carbons of opposite sides is 3.19 Å, which is much shorter than the sum of the van der Waals radii (3.40 Å).¹⁶

The observed deformation as well as intramolecular π-π interaction seem to be responsible for raising the HOMO level of 1 (*E*^{ox} +0.78 V vs. SCE in MeCN; 2e process) compared with 2 (+1.00 V). In fact, oQDM was easily oxidized to reproduce dication 1²⁺, which was isolated as BF₄[−] or SbCl₆[−] salt in 78% and 87% respective yield upon treatment with 2 equivalents of NOBF₄ or (4-BrC₆H₄)₃N⁺SbCl₆[−]. The reduction potential of 1²⁺ was observed in the far cathodic region (+0.28 V), and the separation by 0.5 V corresponds to the electrochemical bistability of this couple. Such a large shift of redox peaks as well as one-wave 2e



Scheme 1 Redox pairs based on the oQDM skeleton.



Scheme 2 Oxidative cyclization of 2 to 1²⁺.

† Electronic supplementary information (ESI) available: ORTEP drawings of 1²⁺ and 2. See <http://www.rsc.org/suppdata/cc/b4/b405837b/>

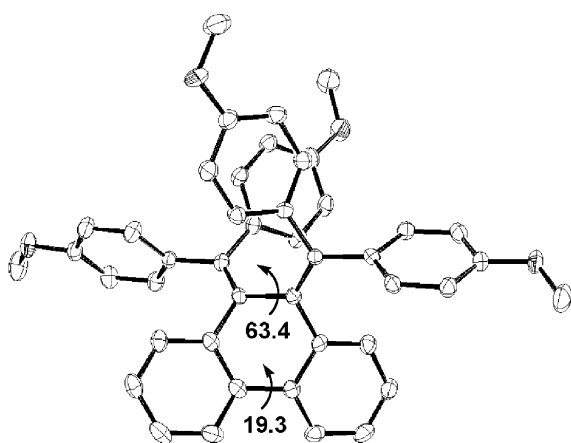


Fig. 1 ORTEP drawing of **1** determined by X-ray analysis of CHCl_3 solvate at -150°C .

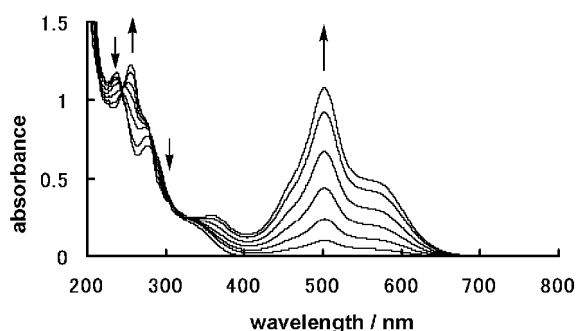


Fig. 2 Continuous changes in the UV-Vis spectrum of **1** (3 mL , $1.52 \times 10^{-5}\text{ mol dm}^{-3}$ in MeCN containing $0.5\text{ mol dm}^{-3}\text{ Bu}_4\text{NBF}_4$) upon constant-current electrochemical oxidation ($28\text{ }\mu\text{A}$, 10 min interval) to $\mathbf{1}^{2+}$.

oxidation process have been commonly observed in the dynamic redox pairs⁵ undergoing reversible C–C bond making/breaking⁴ or drastic structural changes.¹⁷ Preliminary X-ray analysis on the dicationic salt $\mathbf{1}^{2+}(\text{I}^-)_2$ suggests that its phenanthrene unit adopts a planar structure.

Not only the geometries but also their colors change drastically during the interconversion between **1** and $\mathbf{1}^{2+}$. Thus, when the electrochemical oxidation of **1** was followed using UV-Vis spectroscopy, the continuous and clean conversion was observed as shown in Fig. 2 with the development of a huge absorption band in the visible region ($\lambda = 400\text{--}650\text{ nm}$), demonstrating that this couple can serve as a new electrochromic material with high electrochemical bistability. Studies on other stable oQDMs are now under way.

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- According to PM3 calculations on model compounds, 9,10-bis(diphenylmethylene)-9,10-dihydrophenanthrene **1'** ($\text{Ar} = \text{Ph}$) has a smaller heat of formation ($192.25\text{ kcal mol}^{-1}$) than the corresponding cyclobutene derivative, 1,2-dihydro-1,1,2,2-tetraphenylcyclobutylphenanthrene **3'** ($208.12\text{ kcal mol}^{-1}$). Although 9,9a-dihydro-9,9,10-triphenylanthracene is much more stable than 7,7,8,8-tetraphenyl-oQDM or 1,1,2,2-tetraphenylbenzocyclobutene,⁶ this is not the case for the dibenzo analogues. The dihydroanthracene-type isomer was predicted to have the higher heat of formation ($216.18\text{ kcal mol}^{-1}$) than **1'** and **3'**, probably due to the steric repulsion between phenyl substituents and fused benzene rings.
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- Physical data of new compounds are as follows. **1**: mp $97\text{--}98^\circ\text{C}$, ^1H NMR (acetone-d_6) δ 7.89 (2 H, d, $J = 7.5\text{ Hz}$), 7.29 (2 H, dd, $J = 7.5, 7.5\text{ Hz}$), 7.14 (2 H, d, $J = 7.5\text{ Hz}$), 6.75–6.83 (16 H, m), 3.84 (6 H, s), 3.72 (6 H, s); UV-Vis (MeCN) λ_{max} 325sh (log ϵ 4.04), 276 (4.67), 239 (4.75) nm. $\mathbf{1}^{2+}(\text{BF}_4^-)_2$: mp $172\text{--}174^\circ\text{C}$, ^1H NMR (CD_3CN) δ 9.07 (2 H, d, $J = 8.4\text{ Hz}$), 7.94 (2 H, dd, $J = 8.4, 8.4\text{ Hz}$), 7.54–7.60 (10 H, m), 7.41 (2 H, d, $J = 8.4\text{ Hz}$), 7.06 (8 H, AA'XX'), 4.03 (12 H, s); UV-Vis (MeCN) λ_{max} 550sh (log ϵ 4.50), 502 (4.76), 366 (4.11), 272 (4.48), 254 (4.65) nm. **2**: mp $191\text{--}192^\circ\text{C}$, ^1H NMR (CDCl_3) δ 7.23 (2 H, d, $J = 7.5\text{ Hz}$), 7.15 (2 H, dd, $J = 7.5, 7.5\text{ Hz}$), 7.06 (4 H, AA'XX'), 6.95 (2 H, dd, $J = 7.5, 7.5\text{ Hz}$), 6.83–6.88 (6 H, m), 6.77 (4 H, AA'XX'), 6.43 (2 H, s), 6.43 (4 H, AA'XX'), 3.79 (6 H, s), 3.70 (6 H, s).
- Crystal data for $\mathbf{1} \cdot (\text{CHCl}_3)_2$: $\text{C}_{46}\text{H}_{38}\text{Cl}_6\text{O}_4$, M 867.52, tetragonal $\bar{1}4$ (No. 82), $a = 27.728(4)$, $c = 11.005(2)\text{ Å}$, $U = 8461.0(1)\text{ Å}^3$, D_c ($Z = 8$) = 1.362 g cm^{-3} , $T = 123\text{ K}$, $\mu = 4.49\text{ cm}^{-1}$. The final R value is 0.052 for 3232 independent reflections with $I > 3\sigma I$ and 509 parameters. Esds for bond lengths and angles are 0.006–0.008 Å and 0.4–0.5° for non-hydrogen atoms. Due to the orientational disorder of the solvent in the crystal, several positional parameters were fixed in the final least-squares cycle. CCDC 237042. Data for **2**: $\text{C}_{44}\text{H}_{38}\text{O}_4$, M 630.78, orthorhombic $Pbca$ (No. 61), $a = 10.1566(7)$, $b = 18.671(1)$, $c = 35.302(2)\text{ Å}$, $U = 6694.5(8)\text{ Å}^3$, D_c ($Z = 8$) = 1.252 g cm^{-3} , $T = 153\text{ K}$, $\mu = 0.79\text{ cm}^{-1}$. The final R value is 0.039 for 4939 independent reflections with $I > 3\sigma I$ and 433 parameters. Esds for bond lengths and angles are 0.002–0.003 Å and 0.1–0.2° for non-hydrogen atoms. The ORTEP drawing of **2** is given as Figure S1 in the ESI. CCDC 237043. See <http://www.rsc.org/suppdata/cc/b4/b405837b/> for crystallographic data in .cif format.
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- Photoirradiation of **1** caused its isomerization to the 9,10-dihydroanthracene skeleton by electrocyclization and a subsequent 1,3-H shift. The details will be published as a full paper in due course.
- The PM3 calculation on 9,10-bis(diphenylmethylene)-9,10-dihydrophenanthrene **1'** reproduced the values for these angles (59.7° and 18.8° , respectively) so nicely that the observed solid-state structure is intrinsic to this skeleton but not due to the crystal packing force.
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- Crystal data: $\text{C}_{44}\text{H}_{36}\text{O}_4\text{I}_6$, M 1390.2, triclinic $\bar{P}1$, $a = 11.502(2)$, $b = 11.612(2)$, $c = 19.688(3)\text{ Å}$, $\alpha = 84.567(4)$, $\beta = 88.131(4)$, $\gamma = 84.500(4)^\circ$, $U = 2604.9(7)\text{ Å}^3$, D_c ($Z = 2$) = 1.773 g cm^{-3} , $T = 293\text{ K}$. Due to the severe disorder of the iodine atoms, the R value is still quite high (11.3%) (Fig. S2, ESI). We are now trying to obtain other dication salts with different counter anions.