Polycyclic Hydrocarbons

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Indeno[2,1-*a*]fluorene: An Air-Stable *ortho*-Quinodimethane Derivative[**]

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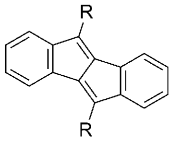
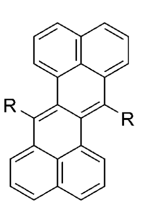
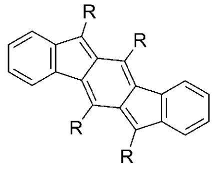
Conjugated polycyclic hydrocarbons[1] have attracted much attention because of their novel fundamental properties and potential application in electronic materials.[2] Recently, thanks to the development of excellent synthetic methods, hydrocarbons with unique electronic structures such as dibenzopentalenes **1**[3] and zethrenes **2**[4] have been subjects of extensive research. In particular, polycyclic hydrocarbons containing a quinodimethane (QDM) structure[5,6] have been studied because of their low-energy bandgaps and excellent electrochemical behavior, which make them potential candidates for optoelectronic materials.



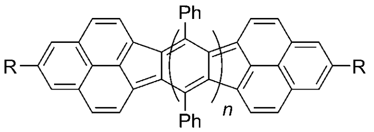
1: R = H, Ph



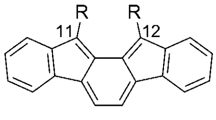
2: R = C≡CPh, H, Bu, Ph, etc.



3a: R = H
3b: R = C≡CTIPS
3c: R = I

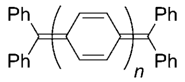


4 (*n* = 1): R = H, Me
5 (*n* = 2): R = H, *t*Bu

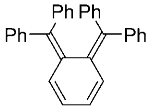


6a: R = H
6b: R = Ph
6c: R = Mes

Very recently, Haley et al. have reported the synthesis and properties of a stable *p*-quinodimethane (*p*QDM) derivative, indeno[1,2-*b*]fluorene **3b** (TIPS = triisopropylsilyl)[5] which was regarded as a fully conjugated 20π-electron hydrocarbon with fused *s-trans* diene linkages across the top and bottom parts of the carbon framework.[7,8] In connection with our own interest in the transannular cyclization of dehydrobenzoannulenes,[9] we became interested in a structural isomer of **3a**, indeno[2,1-*a*]fluorene (**6a**), which possesses an *o*-quinodimethane (*o*QDM) structure instead of the *p*QDM moiety of **3a**, for two reasons: 1) Since *o*QDM[10] has a smaller HOMO–LUMO energy gap than *p*QDM,[11] the HOMO–LUMO gap of **6a** would be smaller than that of **3a**. 2) In contrast to the *p*QDM derivatives, studies on compounds containing an *o*QDM structure are scarce because of their high reactivity due to the *s-cis* diene unit.[12] In fact, studies on *p*QDM-type hydrocarbons such as Thiele's hydrocarbon **7**[13] and Chichibabin's hydrocarbon **8**,[14] which are stable enough to be isolated as crystals,[15] were performed over a century ago. On the other hand, molecules containing the *o*QDM structure, such as tetraphenyl-*o*QDM **9**[16] and pleiadene (**10**)[17] are reported to be highly reactive. These compounds were generated and detected in rigid glass matrices but could not be isolated. Though tetraaryl-*o*QDM **11**[18] and a highly reactive *o*QDM derivative **12**[19] were recently synthesized and isolated, the fundamental properties originating from the *o*QDM moiety remain to be clarified. In this regard, indeno[2,1-*a*]fluorene (**6a**) is an intriguing molecule because the benzo bridge to the *o*QDM structure would not only extend the length of the π-conjugated carbon framework but also prevent one of the typical reactions of *o*QDMs, cyclization to form benzocyclobutenes. Additionally, the fact that **6a** contains an antiaromatic *as*-indacene moiety, which has not been isolated to date,[20] also makes **6a** a fascinating hydrocarbon.



7 (*n* = 1), **8** (*n* = 2)



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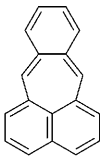

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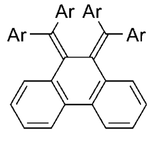
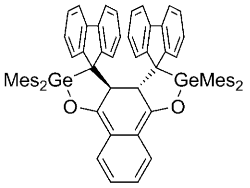


11: Ar = 4-MeOC$_6$H$_4$



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Le Berre et al. synthesized the 11,12-diphenyl derivative **6b**[21] which exhibited an absorption maximum at 556 nm. However, **6b** turned out to be highly reactive toward oxygen[22] and therefore its molecular structure and detailed electronic structures, such as electrochemical behavior and ring-current effect, have not been investigated. In addition, a series of reports by Le Berre et al. in the mid-1950s are the

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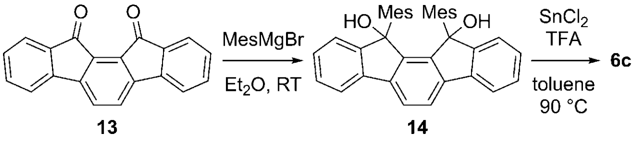
only experimental descriptions of this hydrocarbon system, and there is merely one report on the theoretical work.[23] In the present study, we synthesized an air-stable derivative, 11,12-dimesitylindeno[2,1-*a*]fluorene (**6c**), of which mesityl groups were introduced owing to the prospect of steric protection, and determined its crystal and electronic structures, and optical as well as electrochemical properties.

Scheme 1 shows the synthetic procedure for **6c**. The known diketone **13**[24] was converted to diol **14**[25] by addition of mesitylmagnesium bromide. Dehydroxylation of **14** with tin(II) chloride in the presence of trifluoroacetic acid gave **6c** as a purple solid. In contrast to the high reactivity of **6b**, **6c** was found to be very stable in the solid state and even in solution under ambient conditions. A dichloromethane solution of **6c** showed no degradation under air and light for a week, and no reaction with maleic anhydride was observed when it was heated in toluene at 100°C under an argon atmosphere.



Scheme 1. Synthesis of **6c**. Mes: 2,4,6-trimethylphenyl, TFA: trifluoroacetic acid.

Recrystallization of **6c** from an acetonitrile solution gave purple prisms suitable for X-ray crystallography. There are two crystallographically independent molecules (molecule A and molecule B; Figure 1).[26] The largest difference between the two molecules is the torsion angles of the *s-cis* diene moiety (1.7° for molecule A, and 15.2° for molecule B). There is no other significant difference between the two molecules, thus we use their mean values in the following discussion (see Table S4 in Supporting Information). The indeno[2,1-*a*]fluorene framework of **6c** is almost planar and the two mesityl groups form a large dihedral angle of approximately 70° with the backbone. Expectedly, the methyl groups sterically shield C11 and C12. There are three possible resonance contributors for **6c**: 1) a [20]annulene with alternating single and double bonds along the periphery, 2) a dibenzo-fused [12]annulene, that is, *as*-indacene with alternating single and double bonds, and 3) a dibenzo-bridged *o*QDM (Figure S6 in Supporting Information).

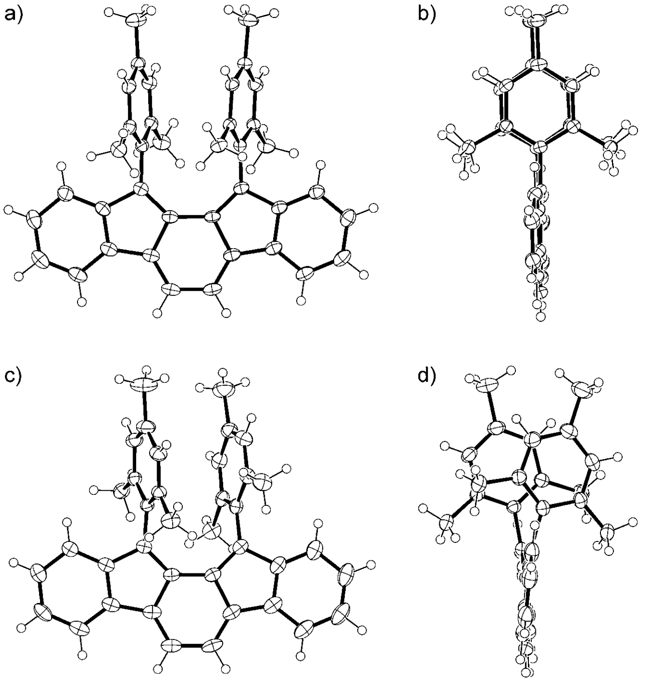


Figure 1. ORTEP drawings of **6c** measured at 113 K: a) top view and b) side view of molecule A, and c) top view and d) side view of molecule B. Displacement ellipsoids are drawn at the 50% probability level.

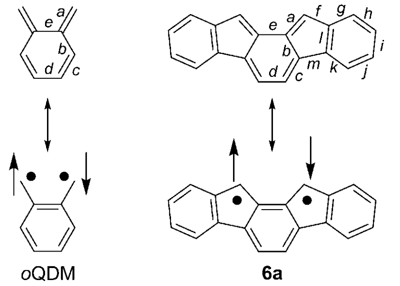
Table 1: Calculated and experimentally determined bond lengths [Å] of the *o*QDM units of **6c**, *o*QDM, and the previously isolated *o*QDMs **11** and **12**.

	Calculated data[b]		X-ray data		
Bond[a]	**6c**	*o*QDM	**6c**[e]	**11**[c]	**12**[d]
a	1.390	1.353	1.391(2)	1.346(6)[e]	1.356(11)[e]
b	1.476	1.462	1.480(2)	1.484(7)[e]	1.448(12)[e]
c	1.362	1.352	1.359(3)	1.417(7)[e]	1.339(12)[e]
d	1.436	1.451	1.431(3)	1.491(7)	1.424(14)
e	1.459	1.497	1.454(2)	1.493(7)	1.475(11)

[a] Bond positions are shown in Scheme 2. [b] Calculated at the RB3LYP/6-31G(d) level. [c] Ref. [18]. [d] Ref. [19]. [e] Mean value.

The crystal structure of **6c** shows that there is significant bond-length alternation in the *o*QDM unit: the bonds denoted by *a* and *c*[27] (1.391(2) and 1.359(3) Å, respectively) have substantial double-bond character, whereas the bonds denoted by *b*, *d*, and *e* (1.480(2), 1.431(3), and 1.454(2) Å, respectively) have single-bond character (Table 1; Scheme). On the other hand, the peripheral benzene rings are delocalized (bonds *g*–*l*, 1.391–1.410 Å), and the bonds denoted by *f* and *m* have single-bond character (1.475(2) and 1.463(3) Å, respectively). These bond lengths show excellent agreement with the theoretical values (Table S4 in Supporting Information) and the previously studied bond orders of **6a**.[23] The geometrical structure of **6c** should therefore be regarded as an *o*QDM bridged with two appended benzene rings.

However, more detailed examination of the bond lengths leads to some modification of the geometrical structures. Bond *a* in **6c** is longer than a regular C(sp^2)–C(sp^2) double bond (1.349 Å),[28] the corresponding bond of *o*QDM calcu-



Scheme 2. Resonance structures of *o*QDM and **6a**.

lated at the RB3LYP/6-31G(d) level of theory, and those of the previously isolated *o*QDMs (**11**: 1.346(6)[18] and **12**: 1.356(11) Å,[19] mean values). The bond-length elongation reminds us of the discussion in connection with Thiele's and Chichibabin's hydrocarbons.[15] Unusual bond lengths in Chichibabin's hydrocarbon were explained in terms of a manifestation of biradical character. Indeed, the singlet biradical character of *o*QDM has been a subject of study.[11d,29] We thus calculated the electronic structure of **6a**. The frontier molecular orbitals of **6a** have large coefficients at C11 and C12 (Figure S7 in the Supporting Information). In addition, the HOMO–LUMO energy gap of **6a** is relatively small (2.25 eV, Table S5 in the Supporting Information). The large spatial overlap between the HOMO and LUMO and small HOMO–LUMO energy gap are characteristic of compounds having singlet biradical character.[30] The singlet biradical character (y) of **6a** and *o*QDM was calculated by the natural orbital occupation number (NOON) of the LUMO in a spin-unrestricted calculation.[31] The broken-symmetry UHF/6-31G(d) calculations of **6a** and *o*QDM gave LUMO occupation numbers of 0.61 and 0.50, respectively. Using the Yamaguchi scheme,[32] the indices for singlet biradical character of **6a** and *o*QDM were estimated to be 0.33 and 0.21, respectively. The spin density distribution of **6a** was calculated at the UBHandHLYP/6-31G(d) level of theory. As in the frontier molecular orbitals, C11 and C12 exhibit the largest spin density of α and β spins, respectively (Figure S10 and Table S6 in Supporting Information). In addition, the spin density distribution of **6a** is quite similar to that of *o*QDM. Based on these theoretical investigations, **6a** should be described as a combination of Kekulé and singlet biradical canonical structures as shown in Scheme 2. The fact that the singlet biradical character of **6a** is more pronounced than that of *o*QDM would be manifested by the elongation of bond *a*, which is most susceptible to the contribution weight of the canonical resonance structure shown in Scheme 2.[33]

The temperature dependence of ^{1}H NMR signals is an experimental indicator of singlet biradical character because a thermally excited triplet species causes broadening of signals. For example, bis-phenalenyl hydrocarbons[6] and anthenes[34] showed signal broadening with an increase in temperature, and the temperature at which the broadening of the signals was observed exhibited a good correlation with the calculated biradical character. However, no temperature dependence was observed in the ^{1}H NMR spectra of **6c** in [D$_6$]DMSO when the solution was heated from 30 to 75 °C (Figures S11 and S12 in the Supporting Information), indicating that the singlet–triplet energy gap of **6c** is relatively large and that the biradical character of **6c** is too small to affect the NMR spectra.[35]

The chemical shifts of **6c** in the ^{1}H NMR spectrum are a good indicator of aromaticity. The protons of **6c** are observed at higher magnetic field than those of **14** (Figures S1 and S3, and Table S7 in Supporting Information). The upfield shift of the protons in the central benzene ring is larger than that of the protons in the peripheral benzene rings by roughly 0.45 ppm. In addition, the Günther Q value[36] of the peripheral benzene ring, which is calculated from the ^3J values of 7.35 and 7.4 Hz, is 1.01; this is smaller than 1.04 and indicates the antiaromatic character of the *as*-indacene moiety. NICS calculation supports the experimental results. The NICS(1) (NICS(1)$_{zz}$[37]) value for the peripheral benzene rings of **6a** is −6.17 (−12.62), which is indicative of aromatic character. Conversely, those for the central benzene ring and five-membered rings are +2.12 (+22.02) and +4.28 (+13.81), respectively, indicating a weak antiaromatic character of the *as*-indacene moiety (Table S8 in Supporting Information).

The optical and electrochemical properties of **6c** suggest that, in spite of the relatively small π conjugation, **6c** has a very small HOMO–LUMO energy gap. The electronic absorption spectrum of **6c** showed low-energy bands at 730 nm ($\varepsilon = 790\,\text{M}^{-1}\text{cm}^{-1}$) and 537 nm ($\varepsilon = 15200\,\text{M}^{-1}\text{cm}^{-1}$; Figure 2). The wavelength of the lowest-energy absorption is longer than that of **3b** (594 nm[5]) and pentacene (582 nm[38]), a representative of hydrocarbons consisting of five fused-ring with a small HOMO–LUMO energy gap. TD-DFT calculations show that both of the bands involve transitions from HOMO to LUMO and HOMO-1 to LUMO (Table S10 in the Supporting Information). The HOMO–LUMO energy gap based on optical properties was thus roughly estimated to be 1.70 eV. Similar to **3**, no fluorescence was observed. The cyclic voltammogram of **6c** exhibits two reversible redox waves ($E^{\text{ox}} = +0.59$ V, $E^{\text{red}} = -1.51$ V (V vs. Fc/Fc$^+$); $E^{\text{redox}} =$ 2.10 V), from which we estimate the electrochemical HOMO–LUMO energy gap of 2.10 eV (Figure S13 in Supporting Information). These values are in good agreement with the calculated value of 2.27 eV.

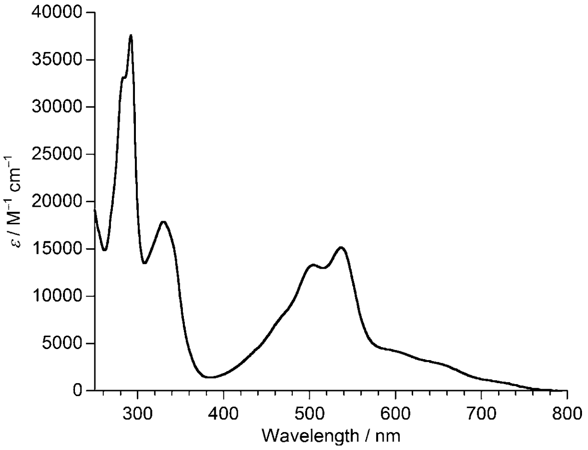


Figure 2. UV/Vis spectrum of **6c** in CH$_2$Cl$_2$.

In conclusion, we have synthesized and isolated an air-stable *o*QDM, 11,12-dimesitylindeno[2,1-*a*]fluorene (**6c**). Examination of the bond lengths indicates that **6c** contains an *o*QDM structure. Detailed examination of the bond lengths and theoretical calculations indicate some singlet biradical character of **6c**. NICS calculation and chemical shifts in the ^{1}H NMR spectrum suggest that **6c** is weakly antiaromatic as a result of the *as*-indacene moiety. Despite the limited π conjugation, **6c** shows low-energy absorptions and excellent electrochemical properties. These findings suggest that indeno[2,1-*a*]fluorene derivatives are potential candidates for optoelectronic materials. We are now investigating the electronic properties of **6c** characteristic of singlet biradicals, such as two-photon absorption.[39]

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[22] In benzene (20 mL), **6b** (5 mg) is reported to decompose within 2.25 h at 21 °C under diffused light and within 4 h at 16 °C in the dark.[21d]

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[25] Only one isomer was obtained and the stereochemistry was not determined.

[26] Crystal data of **6c**: Formula $(C_{38}H_{32})_4CH_3CN$, $M_r = 1995.60$, $0.4 \times 0.1 \times 0.1\ \text{mm}^3$, $T = 113(2)$ K, monoclinic, space group $C2/c$, $a = 38.228(2)$ Å, $b = 19.3674(10)$ Å, $c = 15.4065(9)$ Å, $\beta = 104.9935(13)°$, $V = 11\,018.2(11)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.203\ \text{g cm}^{-3}$, $\mu = 0.068\ \text{mm}^{-1}$, $F(000) = 4248$, $2\theta_{\max} = 54.80°$, R_1 $(I > 2\sigma(I)) = 0.0545$, wR_2 (all data) = 0.1319 and GOF = 1.023 for 12 450 reflections and 713 parameters. CCDC 817811 contains 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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and 2,3,6,7-tetrahydro-1,8-dimesityl-*as*-indacene (**15b**) ($y=0.18$) (Table S4 in Supporting Information). The calculated lengths of bond *a* in *o*QDM and **15a** are quite similar, indicating the effect of the five-membered ring is negligibly small. The comparison of the bond lengths in **6a** and **6c**, or **15a** and **15b** indicates that the steric repulsion between the mesityl groups elongates the bond *a* by about 0.015 Å. X-ray analysis shows that bond *a* in **6c** is longer than that in previously isolated *o*QDMs, **11** and **12** by 0.045, and 0.035 Å, respectively. Thus the elongation of about 0.02 Å would be due to the increase of the singlet biradical character.

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