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Synthesis, Physical Properties, and Crystal Structure of Acetetracenylene-1,2-dione

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Acetetracenylene-1,2-dione was synthesized by double Friedel–Crafts acylation of tetracene with oxalyl chloride in 46–54% yield. Photophysical, electrochemical, and thermal analysis of the compound revealed its band gap ($E_g = 1.77$ eV for the solid state), electron-accepting nature ($E_{pc}{}^{red} = -1.35$ V vs. Fc/Fc^+), and thermal stability ($T_{decomp} > 300$ °C). Single crystals were successfully grown by physical vapor transport, and parallel π-stacking of the molecules was observed by X-ray crystallography.

Aromatic ketones are important chemicals that have been widely used in the textile, pharmaceutical, cosmetic, and agrochemical industries. Among them, diketone derivatives of acenes are useful intermediates for synthesizing polycyclic aromatic hydrocarbon derivatives for textile dyes,[1] antitumor agents,[2] and bidentate ancillary ligands of polymerization catalysts.[3] The diketone moiety is a versatile starting unit for preparing useful functionalities such as carboxylic acid anhydrides,[1] carbodiimides,[1] and α-diimines,[3] which can be used to control molecular dipole moment, solubility, and HOMO and LUMO levels to make compounds suitable for practical uses. Acenaphthylene-1,2-dione (also called acenaphthoquinone) and aceanthrylene-1,2-dione[4] (Figure 1) have been widely used for such purposes. In particular, aceanthrylene-1,2-dione has received special attention as a starting material for constructing near-infrared dyes[5] because it has a more extensive π-conjugated system. Although a much more delocalized π-system can be expected to provide richer functionality, acetetracenylene dione has yet to be synthesized[6] and structurally characterized, likely because of concerns about poor solubility. Herein we report the synthesis of cyclopenta[*fg*]tetracene-1,2-dione (acetetracenylene-1,2-dione) (Figure 1), a diketone derivative of tetracene, as well as its physical properties and X-ray crystal structure. The present compound can be expected to serve as a useful intermediate for expanding the above-mentioned applications.

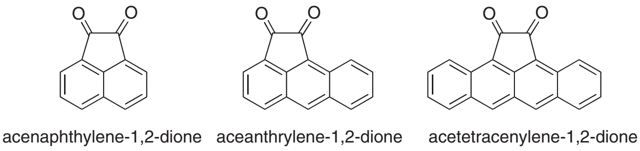
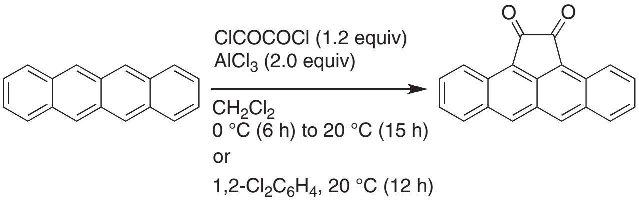


Figure 1. Diketone derivatives of acenes.



Scheme 1. Synthesis of acetetracenylene-1,2-dione.

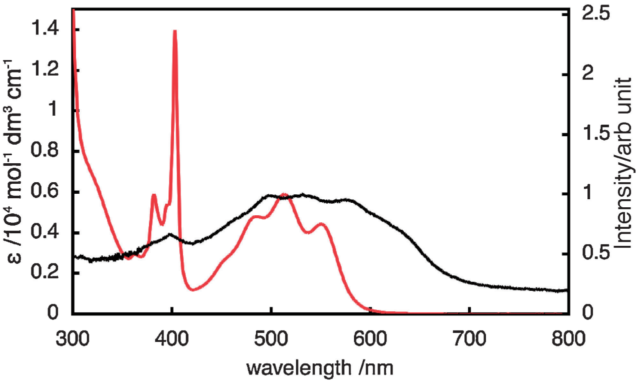


Figure 2. UV–vis spectra of acetetracenylene-1,2-dione in $CHCl_3$ (9.2×10^{-5} M; red line) and in the solid state (properly diluted with $BaSO_4$; black line).

The synthesis employs double Friedel–Crafts acylation with oxalyl chloride, which has been reported for preparing acenaphthoquinone and aceanthrylene diones.[5] We applied this reaction to tetracene to synthesize the target acetetracenylene-1,2-dione (Scheme 1). After considerable experimentation, the optimized reaction conditions were the use of 1.2 molar equivalents of oxalyl chloride and 2.0 molar equivalents of $AlCl_3$ in CH_2Cl_2 at 0 °C for 6 h, followed by stirring of the reaction mixture at 20 °C for 15 h. Most of the tetracene was consumed under the optimized conditions. After removal of aluminum compounds by washing with a 9:1 mixture of MeOH and aq. HCl, purification by sublimation was performed under vacuum (≈0.007 Torr) at 220 °C for 15 h to obtain the pure target compound. The chemical yield after sublimation was respectable (46% yield).[7] Alternatively, by using *ortho*-dichlorobenzene which has higher solubility for tetracene, the reaction proceeded in quantitative conversion of tetracene. Under these conditions, the analytical pure target compound was obtained in 54% yield without sublimation purification.[8] The product was identified by ^1H and ^{13}C NMR, IR spectroscopy (Figure S1[17]), and elemental analysis. The compound formed air-stable, black crystals and dissolved in CH_2Cl_2, $CHCl_3$, $1,2\text{-}Cl_2C_6H_4$, dimethyl sulfoxide, and other organic solvents to give a reddish solution.

The photophysical properties of acetetracenylenedione were investigated by UV–vis and fluorescence spectroscopy. The UV–vis spectrum in chloroform exhibited absorption maxima at $\lambda = 550$ ($\varepsilon = 4.4 \times 10^3$; onset: $\lambda = 585$ nm, 2.12 eV), 513 ($\varepsilon = 5.9 \times 10^3$), and 484 nm ($\varepsilon = 4.8 \times 10^3$) along with sharp peaks at 403 ($\varepsilon = 1.4 \times 10^4$) and 382 nm ($\varepsilon = 5.9 \times 10^3$)

(Figure 2). Absorption of acetetracenylenedione was found to be red-shifted with ca. 80 nm (absorption maxima) and ca. 100 nm (onset) from that of aceanthrylene-1,2-dione (Figure S2[17]). In the solid state, the compound exhibited broad and red-shifted absorption at $\lambda = 575$, 533, and 496 nm with a red-shifted onset value ($\lambda =$ ca. 700 nm). The band gap, E_g, for the solid state was calculated from the absorption onset to be 1.77 eV. The compound was not fluorescent.

The electrochemical properties of acetetracenylene-1,2-dione were investigated by cyclic voltammetry. Oxidation of the acetetracenylenedione was not observed in the potential window of dichloromethane, suggesting that the two strongly electron-withdrawing carbonyl groups result in the tetracene core being electron-deficient. This compound exhibited an irreversible reduction wave at $E_{pc} = -1.35$ V and $E_{onset} = -1.25$ V vs. Fc/Fc$^+$ in dichloromethane (Figure S3[17]). From the reduction wave, we roughly estimated the LUMO level to be −3.55 eV.[9,10] This value is comparable to reported electron-deficient acenes with fluoro- or cyano substitution.[11] In addition, the value is similar or higher than that of electron-accepting materials such as fullerene derivatives, C_{60}–bis(indene) adduct (ICBA, −3.63 eV)[12,13] and bis(silylmethyl)[60]fullerene (−3.74 eV),[14] which are known to be fullerene-based acceptors with high-lying LUMO levels and used in organic photovoltaic cells to obtain high open-circuit voltage.[15]

The thermal properties of the acetetracenylenedione were investigated by thermogravimetry-differential thermal analysis (TG-DTA) under nitrogen. The compound did not exhibit any weight loss until 300 °C. A sharp endothermic peak was observed at 370 °C in the DTA curve (Figure S5[17]). We can conclude that this compound has sufficient thermal stability, even under ambient pressure, for various applications.

Single crystals of acetetracenylene-1,2-dione were prepared by physical vapor transport using a two-zone (290/190 °C) electrical heating furnace with atmospheric pressure argon gas flow (10 mL min^{-1}). Plate single crystals with metallic luster grew under these conditions, and the crystals were subjected to X-ray crystallographic analysis (Figure 3).[16] The crystal packing of the compound consisted of parallel π-stacking. The interplanar distance between tetracene planes was 3.36 Å, shorter than the sum of the C···C van der Waals radii (3.40 Å). The molecules align to form polar arrays, which are oriented in an antiparallel manner so that the dipole moments cancel (Figures 3c and 3d). Such structures are quite different from the packing structure of a less π-delocalized compound, aceanthrylene-1,2-dione, which forms herring-bone packing (Figure S6[17]).

In conclusion, we successfully carried out double Friedel–Crafts acylation of tetracene with oxalyl chloride to obtain acetetracenylene-1,2-dione, which should be a useful intermediate for further derivatization to produce various fine chemicals. Compared with known naphthalene and anthracene diketone derivatives, the present tetracene diketone derivative is expected to provide richer functionality resulting from its more delocalized π-conjugated system. We elucidated its photophysical properties, electron-accepting nature, and thermal stability as well as its parallel π-stacking structure. This information will be useful for not only further functionalization but also application of the acetetracenylenedione itself in organic thin-film devices.[18] Such investigations are underway.

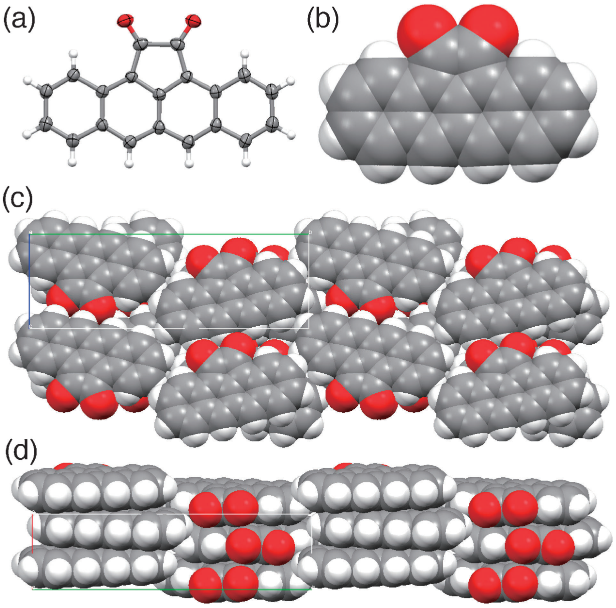


Figure 3. Crystal structure of acetetracenylene-1,2-dione. (a) Ellipsoidal drawing showing the 50% probability level. (b) Space-filling model. (c) Packing structure viewed along the *a* axis. (d) Packing structure viewed along the *c* axis.

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7 Black microcrystals. Melting point was not available due to sublimation at 300 °C under ambient pressure. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.14 (d, $J = 9.15$ Hz, 2H), 9.04 (s, 2H), 8.18 (d, $J = 8.60$ Hz, 2H), 7.79 (t, 2H), 7.63 (t, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 188.96, 139.92, 138.69, 134.04, 133.73, 131.06, 130.44, 128.30, 127.44, 124.84, 102.79. IR (powder), ν_{CO}: 1698 cm^{-1} (s). Anal. Calcd for

$C_{20}H_{10}O_2$: C, 85.09; H, 3.57%. Found: C, 84.81; H, 3.57%.

8 Details are described in Supporting Information.

9 LUMO levels were estimated with the following equation: LUMO level $= -(4.8 + E_{\mathrm{onset}})$ eV.

10 Aceanthrylene-1,2-dione showed a reversible reduction wave at $E_{1/2} = 1.39$ V vs. Fc/Fc$^+$. Cyclic voltammogram has been stored in Supporting Information (Figure S4).[17]

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12 A LUMO level has been determined from the first reduction potential in our investigation with the following equation: LUMO level $= -(4.8 + E_{1/2})$ eV.

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16 Crystal data for acetetracenylene-1,2-dione: monoclinic space group $P2_1/a$, $a = 6.8111(1)$, $b = 23.4800(5)$, $c = 8.5200(2)$ Å, $\beta = 110.906(1)°$, $Z = 4$, $V = 1272.85(4)$ Å^3. $R = 0.0958$ ($I > 2\sigma(I)$). GOF $= 1.464$.

17 Although there are many reports of aceanthrylene-1,2-dione, its crystal structure has not been reported. Crystal data for aceanthrylene-1,2-dione: triclinic space group $P\bar{1}$, $a = 8.5161(2)$, $b = 13.1515(2)$, $c = 19.0360(4)$ Å, $\alpha = 94.8259(8)$, $\beta = 100.3680(8)$, $\gamma = 101.4892(8)°$, $Z = 2$ (for a pair of four independent molecules), $V = 2039.19(6)$ Å^3. $R = 0.0741$ ($I > 2\sigma(I)$). GOF $= 0.914$. Detailed structural data are stored in Supporting Information (synthetic procedures, IR and UV spectra, cyclic voltammogram, and TG-DTA data as well as X-ray crystallographic data for acetetracenylene-1,2-dione and aceanthrylene-1,2-dione). Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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