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Journal of Sulfur Chemistry

Publication details, including instructions for authors and subscription information:

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To cite this Article Sato, Ohki , Sato, Makoto , Sugimoto, Hiroshi , Kuramochi, Takaaki , Shirahata, Takashi and Takahashi, Kazuko(2009) 'One-pot synthesis of bromo-tetracyanoazulenequinodimethanes and conducting properties of their charge transfer complexes with tetrathiotetracene', *Journal of Sulfur Chemistry*, 30: 3, 360 – 364

To link to this Article: DOI: 10.1080/17415990902930390

URL: <http://dx.doi.org/10.1080/17415990902930390>

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One-pot synthesis of bromo-tetracyanoazulenequinodimethanes and conducting properties of their charge transfer complexes with tetrathiotetracene

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(Received 2 February 2009; final version received 28 March 2009)

This paper is dedicated to Professor Juzo Nakayama on the occasion of his 65th birthday and retirement.

Bromo-tetracyanoazulenequinodimethanes have been synthesized by the one-pot reaction of 1,3,5-tribromoazulene with tetracyanoethylene oxide. These electron acceptors formed corresponding charge transfer complexes with tetrathiotetracene, some of which were shown to have conducting ability.

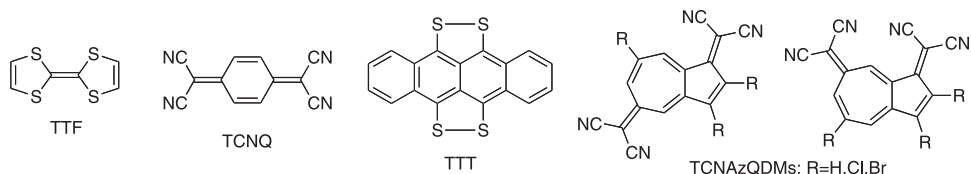
Keywords: tetracyanoazulenequinodimethane; one-pot synthesis; charge transfer complex; tetrathiotetracene; conducting ability

1. Introduction

Since the high electrical conductivity of charge transfer (CT) complex with tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ) was reported in 1973 (1), interest in organic conductors was accelerated. Although many strong electron donors such as TTF derivatives and tetrathiotetracene (TTT) have been synthesized, far less electron acceptors with new frameworks (2–4) seem to have been developed, except for a considerable number of the benzenoid TCNQ family. Especially, as for the non-benzenoid system, the syntheses of 2,4,6,8-tetracyanoazulene (5), [3]radialene type acceptor (6) and *N,N'*-dicyano-*p*-acepleiadylenequinonediiimine (7) have been reported so far. Tetracyanoazulenequinodimethanes (TCNAzQDMs) (8) are novel non-benzenoid acceptor series, which have been synthesized by the reaction of azulenequinone (9, 10) with Rehnart reagent (11, 12) in our laboratory, and are expected for a component of conducting CT complexes. However, the many synthetic steps for them and the resulting low yields dissuaded us from the application for organic conductors.

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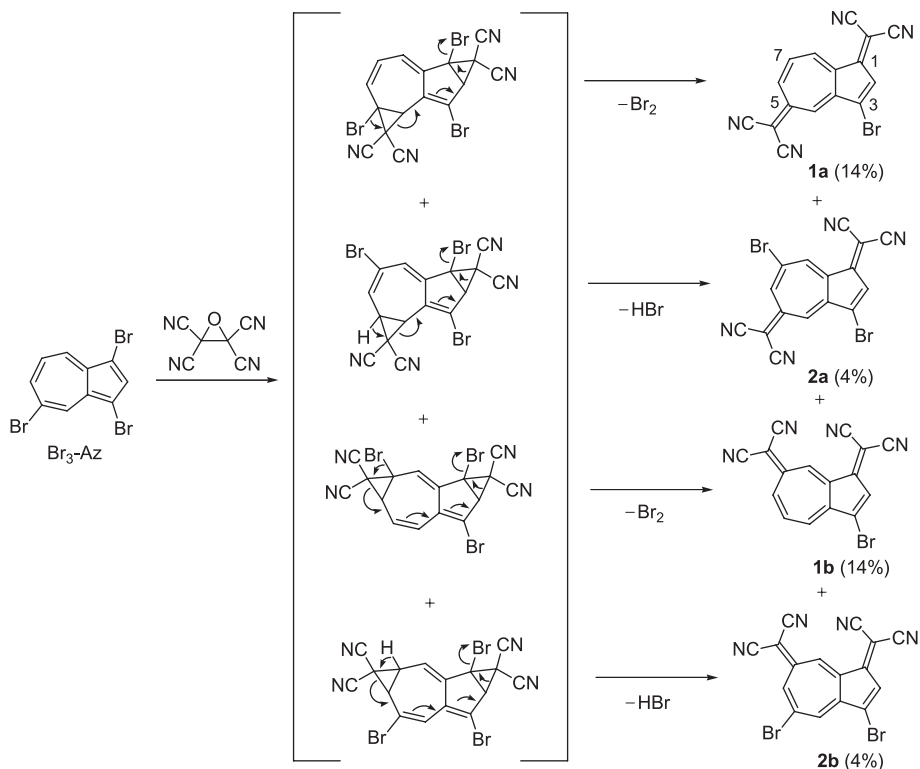
In this context,¹ we present the one-pot synthesis of bromo-TCNAzQDMs **1a**, **1b**, **2a** and **2b** from 1,3,5-tribromoazulene ($\text{Br}_3\text{-Az}$) (**9**, **10**), and some conducting abilities of their CT complexes with TTF.



2. Results and discussion

2.1. One-pot synthesis of bromo-TCNAzQDMs

1,3,5-Tribromoazulene, derived from the reaction of azulene with pyridinium tribromide in boiling benzene (**9**, **10**), was treated with tetracyanoethylene oxide (TCNEO) (**13**) in hot 1,2-dibromoethane to give a mixture of 3-bromo-1,5-TCNAzQDM **1a**, 3,7-dibromo-1,5-TCNAzQDM **2a**, 3-bromo-1,7-TCNAzQDM **1b** and 3,5-dibromo-1,7-TCNAzQDM **2b** in 14, 4, 14 and 4% yields, respectively (Scheme 1). Their spectral and physical data were in agreement with the values in the literature (**8**). The reaction mechanism should involve the formation of dicyclopropane intermediates and the successive rearrangement with elimination of Br_2 or HBr , as



Scheme 1.

shown in Scheme 1. Similar cyclopropanation/rearrangement reaction of 2,5-dibromothiophene with TCNEO was reported (14).

2.2. Preparation and conducting abilities of TCNAzQDM-TTT complexes

Although attempted preparation of the CT complexes of synthetic TCNAzQDMs **1** and **2** with TTF was unsuccessful, 3-bromo-1,5-TCNAzQDM **1a** formed a 1:2 CT complex with TTT (**1a**)[TTT]₂ on mixing each component in 1,2,4-trichlorobenzene (TCB). **1a**)[TTT]₂ was black powder and showed a low room temperature conductivity, measured by four probe method, of $3.0 \times 10^{-6} \text{ S cm}^{-1}$ (as shown in Table 1). In the case of 3-bromo-1,7-TCNAzQDM **1b**, two types of complexes (**1b**)[TTT]₂[TCB]_{0.5} as black powder and **1b**]₂[TTT] as black fine plates) were formed, depending on the concentration. The former was obtained from a solution of $5.0 \times 10^{-3} \text{ mol/L}$, whereas the latter from a solution of $1.7 \times 10^{-3} \text{ mol/L}$. Although the latter was an insulator, the former showed a fairly high conductivity of $5.3 \times 10^{-2} \text{ S cm}^{-1}$ at room temperature. **1b**)[TTT]₂[TCB]_{0.5} exhibited a very broad intra-stack CT absorption band centered at around 3000 cm^{-1} , indicating that this complex exists in a segregated stacking mode in a mixed valence state (15, 16). As shown in Figure 1, **1b**)[TTT]₂[TCB]_{0.5} showed

Table 1. Appearances, IR data and conductivities of the CT complexes.

Compound	Appearance	$\nu \text{ cm}^{-1}$	$\sigma \text{ S cm}^{-1}$
1a)[TTT] ₂	Black powder	2205 ^a	3.0×10^{-6}
1b)[TTT] ₂ [TCB] _{0.5}	Black powder	3000(br) ^b 2208 ^a	5.3×10^{-2}
1b] ₂ [TTT]	Black fine plates	2213 ^c 2205 ^c	$< 10^{-6}$
2b)[TTT]	Black fine plates	2196 ^a	3.8×10^{-3}

Notes: ^aCN stretching absorption appeared as only one signal because of probable overlapping. ^bCT absorption. ^cCN stretching absorption.

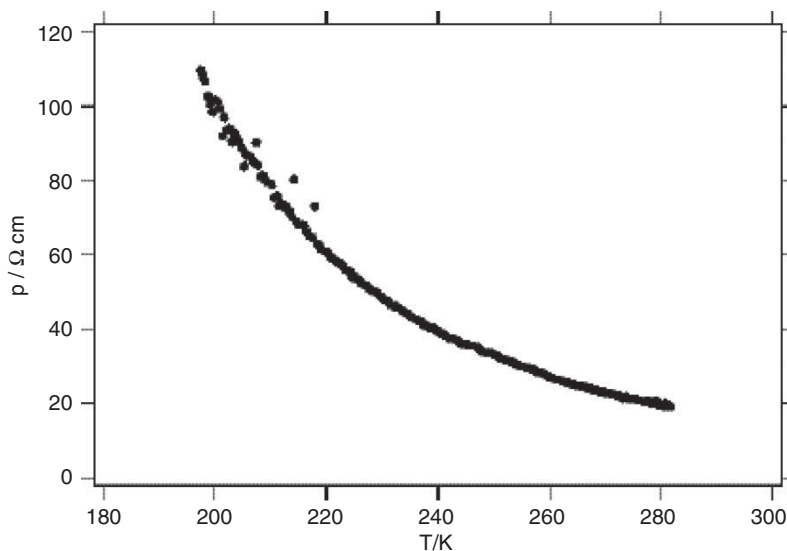


Figure 1. Temperature dependency of the resistivity of **1b**)[TTT]₂[TCB]_{0.5}.

semiconducting temperature dependence from room temperature down to 200 K, with activation energy of 9.9×10^{-2} eV. The composition of CT complex (black powder) of 3,7-dibromo-1,5-TCNAzQDM **2a** with TTT was not clear by measurement of elemental analysis. On the other hand, the reaction of 3,5-dibromo-1,7-TCNAzQDM **2b** with TTT afforded a 1:1 complex (**2b**][TTT]), which was black violet fine needles and showed a room temperature conductivity of 3.8×10^{-3} S cm⁻¹. Although the Torrance V-shape correlation (17) has been used to discuss the ionicities of the components in CT complexes, it could not be applied to the present complexes because redox potentials of TTT were not determined due to its insolubility in any solvents at room temperature.

3. Conclusion

In conclusion, we have succeeded in the one-pot synthesis of new azulene-based electron acceptors, bromo-tetracyanoazulenequinodimethanes. These acceptors formed some conducting CT complexes with TTT. Preparation of single crystalline CT complexes for X-ray analysis is in progress, to obtain more information on the relationships between conductivity and packing structure.

4. Experimental

4.1. General

Mps were determined with a Mitamura air-bath apparatus and are uncorrected. ¹H and ¹³C NMR spectra (SiMe₄ as the internal standard) were obtained with Bruker AC-200 and/or AC-300 spectrometers. IR spectra were obtained with a Perkin Elmer System 2000 FT instrument. MS spectra were obtained with JEOL JMS700AM spectrometers. Unless otherwise stated, the spectra were taken in the following solvents/media: IR, KBr; ¹HNMR (200 and 300 MHz), CDCl₃; MS spectra were taken at 70 eV by electron impact (EI) and fast atom bombardment (FAB) method. The progress of reactions was followed by TLC method using Merck Silica gel 60F₂₅₄. The conductivities (resistivities) of the CT complexes were measured by the four probe method on using a YOKOGAWA 7651 programmable direct current source and a KEITHLEY 2001 digital multimeter unit. Gold wires (10 or 15 μm diameter) were attached to the complexes with carbon paste.

4.2. Synthesis of bromo-tetracyanoazulenequinodimethanes **1a**, **1b**, **2a** and **2b**

To a boiling solution of 1,3,5-tribromoazulene (51 mg, 0.14 mmol) in 3.6 mL of 1,2-dibromoethane, 40 mg (0.22 mmol) of tetracyanoethylene oxide (content of 80%) (13) was added under N₂. The reaction mixture was boiled for 15 min and the solvent was removed *in vacuo*. The residue was purified by neutral SiO₂ column chromatography (eluted by *n*-hexane/benzene) to give **1a** (6.4 mg, 14%), **1b** (6.5 mg, 14%), **2a** (2.3 mg, 4%) and **2b** (2.3 mg, 4%), respectively. Corresponding spectral and physical data of the obtained compounds were in agreement with the values in the literature (8).

4.3. General procedure for preparation of tetracyanoazulenequinodimethanes-tetrathiotetracene complexes

A hot solution of bromo-tetracyanoazulenequinodimethane **1a**, **2a**, **1b** or **2b** (3.0×10^{-2} mmol) in 1,2,4-trichlorobenzene (3.0 or 9.0 mL) was mixed with a hot solution of tetrathiotetracene

(6.0×10^{-2} mmol) in 1,2,4-trichlorobenzene (3.0 or 9.0 mL) at 150 °C, and then a mixture of the solution was left to stand for 3 d at room temperature. The resulting precipitate (charge transfer complex) was filtered and washed with 1,2,4-trichlorobenzene, EtOH and *n*-hexane. The NMR and electronic spectra of the complexes could not be measured because of their insolubility in any solvent.

[**1a**][TTT]₂ complex: Yield 77%, black powder, mp >300 °C, IR(KBr) ν 2205 (CN) cm⁻¹, Anal. Calcd for C₅₂H₂₁BrN₄S₈: C, 60.16; H, 2.04; N, 5.40. Found: C, 59.99; H, 1.80; N, 5.11, σ_{rt} 3.0×10^{-6} S cm⁻¹.

[**1b**][TTT]₂[TCB]_{0.5} complex: Yield 48%, black powder, mp >300 °C, IR(KBr) ν 3000 (br, CT), 2208 (CN) cm⁻¹, Anal. Calcd for C₅₅H_{22.5}BrCl_{1.5}N₄S₈: C, 58.52; H, 2.01; N, 4.96. Found: C, 58.73; H, 1.86; N, 4.69, σ_{rt} 5.3×10^{-2} S cm⁻¹. Temperature-dependent resistivities were measured by four probe method at 200–280 K. Their values were plotted as shown in Figure 1.

[**1b**]₂[TTT] complex: Yield 20%, black fine plates, mp >300 °C, IR(KBr) ν 2213 (CN), 2205 (CN) cm⁻¹, Anal. Calcd for C₅₀H₁₈Br₂N₈S₄: C, 58.95; H, 1.78; N, 11.00. Found: C, 59.05; H, 1.69; N, 10.82, σ_{rt} < 10^{-6} S cm⁻¹.

[**2b**][TTT] complex: Yield 82%, black violet fine needles, mp >300 °C, IR(KBr) ν 2196 (CN) cm⁻¹, Anal. Calcd for C₃₄H₁₂Br₂N₄S₄: C, 53.41; H, 1.58; N, 7.33. Found: C, 53.20; H, 1.47; N, 7.17, σ_{rt} 3.8×10^{-3} S cm⁻¹.

Note

1. A part of this paper was reported for the 21st International Symposium on the Organic Chemistry of Sulfur (2004, Madrid); for the Proceedings, see *Phosphorus, Sulfur and Silicon and Related Elements* **2005**, 180, 1483–1484.

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