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## AZULENE-BASED TETRATHIAFULVALENES: PREPARATION AND THEIR ELECTRON-DONATING ABILITY

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**Abstract** – The condensation reaction of dithiocarbonates derived from azuleno- and guaiazulenopentathiepin with vinylene trithiocarbonate and the ethylenedithio derivative in triethyl phosphite afforded azulene-based tetrathiafulvalenes [Az-TTF, Az-(EDT)TTF, GAz-TTF and GAz-(EDT)TTF], respectively. The vinylene derivatives (Az-TTF and GAz-TTF) showed slightly higher electron-donating ability than the corresponding ethylenedithio ones [Az-(EDT)TTF and GAz-(EDT)TTF] by CV measurement. GAz-TTFs produced charge transfer complexes with tetracyanoquinodimethane, respectively.

Azulene (**1**) and guaiazulene (**2**) are familiar non-benzenoid aromatics having polarized structures, and their chemical, physical and biological properties are of interest.<sup>1</sup> Particularly, electrochemical properties of azulene derivatives much attracted our attention. In the field of electron acceptors, we had already reported azulene-based acceptors such as azulenequinones<sup>2</sup> and tetracyanoazulenequinodimethanes.<sup>3</sup> Next our interest is focused on azulene-based electron donors. Azulenes with sulfur groups should be expected to the key compounds for their construction, whereas the synthetic methods have not been much investigated.<sup>4</sup> Recently we have reported the preparation and properties of azulenopentathiepin (**3**)<sup>5</sup> and its guaiazulene derivative (**4**).<sup>6</sup> These pentathiepins could be transformed to 1,2-*S*-substituted azulenes such as dithiocarbonates (**5** and **6**).<sup>5,6</sup>

Tetrathiafulvalenes (TTFs) are the mostly familiar organic electron donors, and much investigation have been carried out<sup>7</sup> since the charge transfer complex with tetracyanoquinodimethane (TCNQ) showed high electrical conductivity.<sup>8</sup>

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This paper is dedicated to Professor Dr. Masakatsu Shibasaki on the occasion of the 70th birthday.



determined because of the some instability to SiO<sub>2</sub>. In the case of the reaction of **5** with ethylenedithio derivative (**8**), the products were azuleno(ethylenedithio)tetrathiafulvalene [**10**: Az-(EDT)TTF, 40% yield] and bis(ethylenedithio)tetrathiafulvalene [(BEDT)TTF].

Az-TTF (**9**) was pale brown solid [mp 160-161 °C (dec.)]. The <sup>1</sup>H NMR spectrum showed five protons at δ 7.02, 7.04, 7.36, 7.64 and 7.89 with an appropriate coupling constant (*J* = 10.0 Hz) as a seven-membered ring moiety of an azulene skeleton and a singlet proton at δ 7.13 as a five-membered one. The vinylene protons were observed at δ 6.37 (2H) as a broad peak. The <sup>13</sup>C NMR spectrum showed thirteen carbons (two carbons were overlapped at δ 118.6), supporting the azulene-TTF skeleton. The longest wave-maximum of UV-VIS spectrum in CH<sub>2</sub>Cl<sub>2</sub> appeared at 642 nm (log ε 2.52) as a characteristic peak of *S*-heterocycle-fused azulenes such as azuleno-1,4-dithiin<sup>5</sup> and a 1,2-dithiin with a guaiazulene skeleton.<sup>6</sup> MS spectra gave a molecular ion peak [FAB: *m/z* 304 (M<sup>+</sup>)]. Together with the results of elemental analysis, those spectral data supported the proposed structure. Az-(EDT)TTF (**10**) was pale brown solid [mp 214-215 °C (dec.)]. The <sup>1</sup>H NMR and <sup>13</sup>C NMR peaks of the ethylenedithio moiety were observed magnetic equivalently at δ 3.32 (4H) and δ 29.7 (2C), respectively. The other instrumental analysis data also supported the proposed structure.

As for the guaiazulene derivative (**6**),<sup>6</sup> the reaction with **7** or **8** under the same conditions as described above afforded guaiazulenotetrathiafulvalene (**11**: GAz-TTF, dark brown solid, mp 131.5-132 °C, 25% yield) or guaiazuleno(ethylenedithio)tetrathiafulvalene [**12**: GAz-(EDT)TTF, pale green solid, mp 156-157 °C, 49% yield] with a by-product [TTF or (BEDT)TTF], respectively. Corresponding physical data of **11** and **12** were consistent with their proposed structures.

Table 1. Redox potentials (E/V)<sup>a</sup> of azulene-based TTFs (**9-12**) and azulenes (**1** and **2**)

Compound	(E <sub>1<sup>red</sup></sub> ) <sub>pc</sub> <sup>b</sup>	(E <sub>1<sup>ox</sup></sub> ) <sub>pc</sub> <sup>c</sup>	(E <sub>1<sup>ox</sup></sub> ) <sub>1/2</sub> <sup>d</sup>	(E <sub>1<sup>ox</sup></sub> ) <sub>pa</sub> <sup>e</sup>	(E <sub>2<sup>ox</sup></sub> ) <sub>pc</sub> <sup>c</sup>	(E <sub>2<sup>ox</sup></sub> ) <sub>1/2</sub> <sup>d</sup>	(E <sub>2<sup>ox</sup></sub> ) <sub>pa</sub> <sup>e</sup>	(E <sub>3<sup>ox</sup></sub> ) <sub>pa</sub> <sup>e</sup>
Az-TTF <b>9</b>	-1.93	-0.13	-0.04	+0.05	+0.10	+0.22	+0.34	+1.30
Az-(EDT)TTF <b>10</b>	-1.92	+0.01	+0.09	+0.17	+0.22	+0.27	+0.33	-
GAz-TTF <b>11</b>	-1.34	-0.15	-0.06	+0.04	+0.11	+0.23	+0.35	+1.09
GAz-(EDT)TTF <b>12</b>	-1.46	-0.01	+0.04	+0.09	+0.22	+0.26	+0.31	+1.12
Az <b>1</b>	-2.10	-	-	+0.59	-	-	-	-
GAz <b>2</b>	-1.24	-	-	+0.40	-	-	-	-

<sup>a</sup> Obtained by cyclic voltammetry: V vs. Ag/Ag<sup>+</sup>, 10<sup>-3</sup> M in DMF with 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>, 100 mV/s. <sup>b</sup> Reduction potentials by the cathodic peak. <sup>c</sup> Oxidation potentials by the cathodic peak. <sup>d</sup> Half-wave oxidation potentials. <sup>e</sup> Oxidation potentials by the anodic peak.

In order to survey the electrochemical properties of azulene-based TTFs (**9-12**), their cyclic voltammetry (CV) was measured (Table 1). All compounds showed one irreversible wave at reduction region ( $E_1^{\text{red}}$ ) and two or three waves at oxidation region [ $E_1^{\text{ox}}$ ,  $E_2^{\text{ox}}$ , ( $E_3^{\text{ox}}$ )]. First and second waves of the latter were reversible ones resulting from a TTF skeleton. The irreversible waves of the former and the latter of third might be originated from an azulene moiety. Compounds (**9-12**) had higher ability than parent azulenes (**1** and **2**) as an electron donor under the influence of their TTF moieties [ $(E_1^{\text{ox}})_{\text{pa}}/V$ : **9**; +0.05, **10**; +0.17, **11**; +0.04, **12**; +0.09 vs. **1**; +0.59, **2**; +0.40]. There was almost no difference of donating ability between the corresponding Az- and GAz-derivatives [ $(E_1^{\text{ox}})_{1/2}/V$ : **9**; -0.04 vs. **11**; -0.06, **10**; +0.09 vs. **12**; +0.04]. In a scope of TTF substituents, azulene-based TTFs (**9-12**) had some lower electron-donating ability than parent TTF [ $(E_1^{\text{ox}})_{1/2}/V$ : -0.10]. The ability of vinylene derivatives (**9** and **11**) was shown slightly higher than that of ethylenedithio ones (**10** and **12**), respectively.

It is expected that TTF derivatives are a useful component as an electron donor for the construction of charge transfer complexes with TCNQ. We tried preparation of charge transfer complexes by the reaction of GAz-TTF (**11**) and GAz-(EDT)TTF (**12**) with TCNQ in  $\text{CH}_2\text{Cl}_2$ . The former afforded black purple solid [**13**, mp 165 °C (dec.)]. The composition inferred from the results of elemental analysis was  $[\text{GAz-TTF}]_5[\text{TCNQ}]_8$ . The degree of charge transfer could be estimated by comparison of an IR peak of the charge transfer complex with peaks of neutral and absolute ionized molecules (e. g., TCNQ; 2227  $\text{cm}^{-1}$  and  $[\text{K}][\text{TCNQ}]$ ; 2183  $\text{cm}^{-1}$  as a CN stretching peak).<sup>10</sup> The IR peak of **13** was shown at 2189  $\text{cm}^{-1}$ , and the estimated value was 0.86. The latter afforded black purple solid {**14**, mp 169 °C (dec.),  $[\text{GAz-(EDT)TTF}]_2[\text{TCNQ}]_3[\text{CH}_2\text{Cl}_2]_2$ , 2208  $\text{cm}^{-1}$ } and the degree of charge transfer was 0.43.

In conclusion, we have succeeded in the preparation of new azulene-based tetrathiafulvalenes (**9-12**), and evaluated their electron-donating ability. Further work, such as the chemical oxidation of **9-12**, crystal structures and conductivity of the charge transfer complexes, and homo-coupling reaction of **5** or **6**, is now under investigation and will appear elsewhere.

## EXPERIMENTAL

Mps were determined with a Laboratory Devices MEL-TEMP apparatus and are uncorrected.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra ( $\text{SiMe}_4$  as the internal standard) were obtained with Bruker AV500, AM400, AV300, AC300 and/or AC200 spectrometers. IR spectra were obtained with a Perkin Elmer System 2000 FT instrument and electronic spectra (UV-VIS) with a JASCO V-560 spectrophotometer. MS spectra were obtained with JEOL JMS700AM and/or Bruker AutoflexIII spectrometers. CV was obtained with an ALS-600 electrochemical measuring apparatus. Unless otherwise stated the spectra were taken in the following solvents/media: IR, KBr; UV-VIS,  $\text{CH}_2\text{Cl}_2$ ;  $^1\text{H}$  and  $^{13}\text{C}$  NMR,  $\text{CDCl}_3$ ; MS spectra were taken at fast atom bombardment (FAB) and/or MALDI-TOF method; CV, V vs.  $\text{Ag}/\text{Ag}^+$ , GC, Pt wire, 0.1 M

Bu<sub>4</sub>NClO<sub>4</sub> in DMF. The progress of reactions was followed by TLC method using Merck Silica gel 60F<sub>254</sub>.

**General procedure for the preparation of azulene-based tetrathiafulvalenes (9-12):** To a solution of azuleno- or guaiazulenodithiocarbonate (**5** or **6**) in triethyl phosphite (0.1 M), 10 molar *equiv.* of a trithiocarbonate (**7** or **8**) was added and stirred for 10-60 min at 110-120 °C under Ar. The reaction mixture was purified by SiO<sub>2</sub> column chromatography and recrystallization to give Az-TTF (**9**), Az-(EDT)TTF (**10**), GAz-TTF (**11**) or GAz-(EDT)TTF (**12**), respectively. The corresponding yield was indicated in Scheme 1.

**Az-TTF (9):** pale brown solid; mp 160-161 °C (dec.); <sup>1</sup>H NMR δ 6.37 (br, 2H), 7.02 (t like, *J* = 10.0 Hz, 1H), 7.04 (t like, *J* = 10.0 Hz, 1H), 7.13 (s, 1H), 7.36 (t like, *J* = 10.0 Hz, 1H), 7.64 (d, *J* = 10.0 Hz, 1H), 7.89 (d, *J* = 10.0 Hz, 1H); <sup>13</sup>C NMR δ 107.9, 114.2, 116.9, 118.6 (2C), 123.3, 124.5, 124.7, 127.5, 132.6, 133.0, 135.8, 145.4, 149.2; UV-VIS (log ε) λ<sub>max</sub> 642 (2.52), 468 (3.26), 316 (4.24), 225 (4.14); CV (V vs. Ag/Ag<sup>+</sup>) (E<sup>red</sup>)<sub>pc</sub> -1.93, (E<sup>ox</sup>)<sub>pc</sub> -0.13, +0.10, (E<sup>ox</sup>)<sub>1/2</sub> -0.04, +0.22, (E<sup>ox</sup>)<sub>pa</sub> +0.05, +0.34, +1.30; MS (FAB, NBA) *m/z* 304 (M<sup>+</sup>). Anal. Calcd for C<sub>14</sub>H<sub>8</sub>S<sub>4</sub>: C, 55.23; H, 2.65. Found: C, 55.40; H, 2.59.

**Az-(EDT)TTF (10):** pale brown solid; mp 214-215 °C (dec.); <sup>1</sup>H NMR δ 3.32 (s, 4H), 7.04 (t like, *J* = 10.0 Hz, 1H), 7.06 (t like, *J* = 10.0 Hz, 1H), 7.14 (s, 1H), 7.39 (t like, *J* = 10.0 Hz, 1H), 7.67 (d, *J* = 10.0 Hz, 1H), 7.92 (d, *J* = 10.0 Hz, 1H); <sup>13</sup>C NMR δ 29.7 (2C), 108.0, 110.7, 113.5, 113.7, 121.2, 123.4, 123.8, 124.7, 127.7, 132.8, 133.3, 136.1, 145.3, 148.5; UV-VIS (log ε) λ<sub>max</sub> 632 (2.91), 469 (3.77), 390 (4.18), 317 (4.69), 280 (4.51); CV (V vs. Ag/Ag<sup>+</sup>) (E<sup>red</sup>)<sub>pc</sub> -1.92, (E<sup>ox</sup>)<sub>pc</sub> +0.01, +0.22, (E<sup>ox</sup>)<sub>1/2</sub> +0.09, +0.27, (E<sup>ox</sup>)<sub>pa</sub> +0.17, +0.33; MS (MALDI, Dithranol) *m/z* 394 (M<sup>+</sup>). Anal. Calcd for C<sub>16</sub>H<sub>10</sub>S<sub>6</sub>: C, 48.70; H, 2.55. Found: C, 48.70; H, 2.54.

**GAz-TTF (11):** dark brown solid; mp 131.5-132 °C; <sup>1</sup>H NMR δ 1.30 (d, *J* = 6.9 Hz, 6H), 2.49 (s, 3H), 2.87 (s, 3H), 2.90 (sep, *J* = 6.9 Hz, 1H), 6.35 (br, 2H), 6.71 (d, *J* = 10.5 Hz, 1H), 7.08 (dd, *J* = 10.5, 2.1 Hz, 1H), 7.65 (d, *J* = 2.1 Hz, 1H); <sup>13</sup>C NMR δ 12.3, 24.6 (2C), 25.9, 36.2, 114.9, 115.5, 118.6, 118.9, 120.6, 125.9, 127.5, 130.8, 130.9, 134.0, 140.9, 141.2, 141.3, 147.3; UV-VIS (log ε) λ<sub>max</sub> 644 (2.95), 459 (3.67), 387 (4.29), 302 (4.68), 237 (4.29); CV (V vs. Ag/Ag<sup>+</sup>) (E<sup>red</sup>)<sub>pc</sub> -1.34, (E<sup>ox</sup>)<sub>pc</sub> -0.15, +0.11, (E<sup>ox</sup>)<sub>1/2</sub> -0.06, +0.23, (E<sup>ox</sup>)<sub>pa</sub> +0.04, +0.35, +1.09; MS (MALDI, Dithranol) *m/z* 374 (M<sup>+</sup>). Anal. Calcd for C<sub>19</sub>H<sub>18</sub>S<sub>4</sub>: C, 60.92; H, 4.84. Found: C, 61.18; H, 4.57.

**GAz-(EDT)TTF (12):** pale green solid; mp 156-157 °C; <sup>1</sup>H NMR δ 1.30 (d, *J* = 7.0 Hz, 6H), 2.48 (s, 3H), 2.85 (s, 3H), 2.93 (sep, *J* = 7.0 Hz, 1H), 3.31 (s, 4H), 6.73 (d, *J* = 10.5 Hz, 1H), 7.11 (dd, *J* = 10.5, 2.0 Hz, 1H), 7.68 (d, *J* = 2.0 Hz, 1H); <sup>13</sup>C NMR δ 12.2, 24.4 (2C), 25.7, 30.2 (2C), 38.0, 113.4, 113.7, 119.6 (2C), 122.1, 125.9, 127.5, 130.9 (2C), 134.1, 140.6, 141.1, 141.2, 146.3; UV-VIS (log ε) λ<sub>max</sub> 636 (2.90), 461 (3.72), 383 (4.30), 314 (4.40), 278 (4.38); CV (V vs. Ag/Ag<sup>+</sup>) (E<sup>red</sup>)<sub>pc</sub> -1.46, (E<sup>ox</sup>)<sub>pc</sub> -0.01, +0.22, (E<sup>ox</sup>)<sub>1/2</sub>

+0.04, +0.26, ( $E^{\text{ox}}$ )<sub>pa</sub> +0.09, +0.31, +1.12; MS (MALDI, Dithranol)  $m/z$  464 ( $M^+$ ). Anal. Calcd for  $C_{21}H_{20}S_6$ : C, 54.27; H, 4.34. Found: C, 54.49; H, 4.03.

**General procedure for the preparation of charge transfer complexes with GAz-TTFs (11, 12) and TCNQ:** To a solution of GAz-TTF (**11**) or GAz-(EDT)TTF (**12**) in  $CH_2Cl_2$  (20-50 mM), 1 molar *equiv.* of TCNQ in  $CH_2Cl_2$  (20-50 mM) was added and stirred for 1 h at rt under Ar. The resulting precipitate was filtrated by suction and washed with hexane and/or  $CH_2Cl_2$  to give charge transfer complex **13** (42% yield) or **14** (46% yield), respectively.

**Charge transfer complex (13, [GAz-TTF]<sub>5</sub>[TCNQ]<sub>8</sub>):** black purple solid; mp 165 °C (dec.); IR  $\nu$  4000 (br), 2189. Anal. Calcd for [GAz-TTF]<sub>5</sub>[TCNQ]<sub>8</sub> ( $C_{191}H_{122}N_{32}S_{20}$ ): C, 65.42; H, 3.51; N, 12.78. Found: C, 64.79; H, 3.18; N, 12.98.

**Charge transfer complex (14, [GAz-(EDT)TTF]<sub>2</sub>[TCNQ]<sub>3</sub>[CH<sub>2</sub>Cl<sub>2</sub>]<sub>2</sub>):** black green solid; mp 169 °C (dec.); IR  $\nu$  5000-4000 (br), 2208. Anal. Calcd for [GAz-(EDT)TTF]<sub>2</sub>[TCNQ]<sub>3</sub>[CH<sub>2</sub>Cl<sub>2</sub>]<sub>2</sub> ( $C_{80}H_{56}Cl_4N_{12}S_{12}$ ): C, 56.13; H, 3.30; N, 9.82. Found: C, 56.80; H, 2.95; N, 9.87.

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