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

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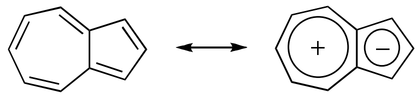
Abstract – The condensation reaction of dithiocarbonates derived from azuleno- and guaiazulenopentathiepin with vinylene trithiocarbonate and the ethylenedithio derivative in triethyl phosphite afforded azulene-based tetrathiafulvalenes [Az-TTF, Az-(EDT)TTF, GAz-TTF and GAz-(EDT)TTF], respectively. The 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.[1] 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[2] and tetracyanoazulenequinodimethanes.[3] 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.[4] Recently we have reported the preparation and properties of azulenopentathiepin (**3**)[5] and its guaiazulene derivative (**4**).[6] These pentathiepins could be transformed to 1,2-*S*-substituted azulenes such as dithiocarbonates (**5** and **6**).[5,6]

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

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



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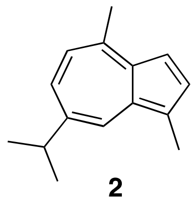

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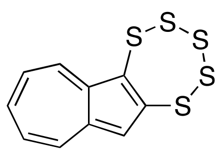

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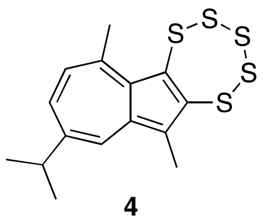

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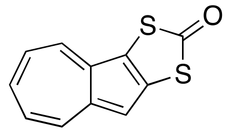

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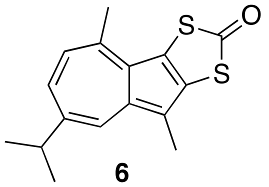

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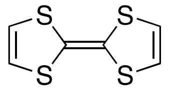
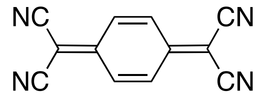


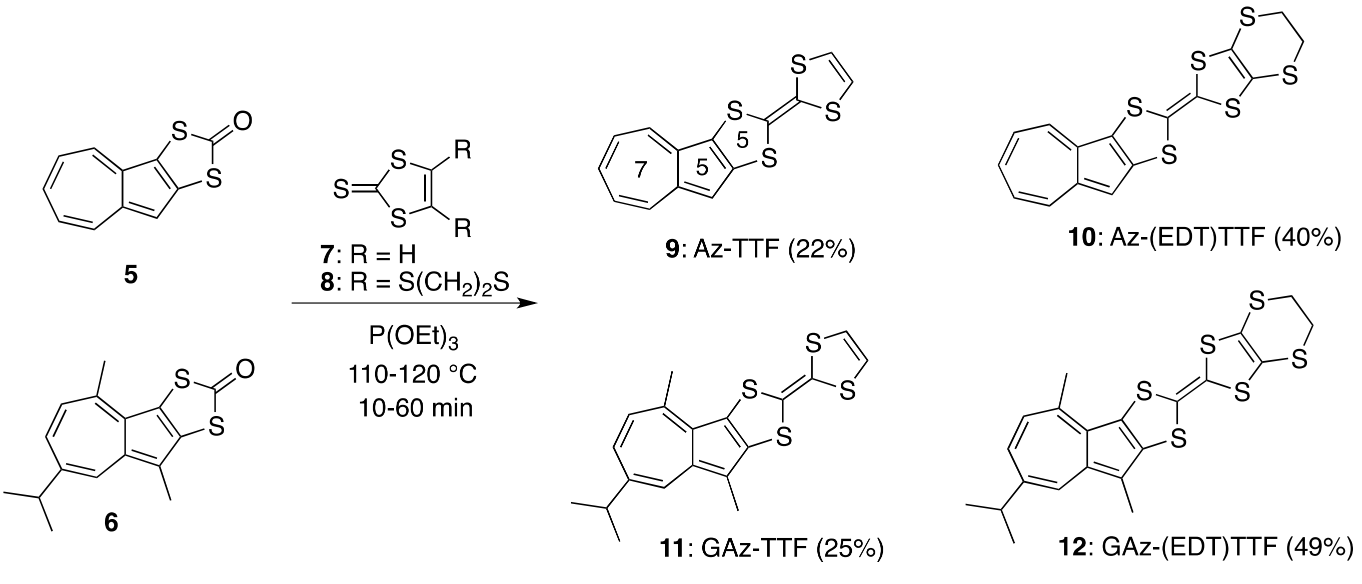
TTF



TCNQ

Even though a few azulenes with TTF moieties have been reported,[9] no compound condensed at the five-membered ring moiety of an azulene skeleton [7-5-5(TTF) type compound, see Scheme 1] is known so far as we are aware. Contribution of the polarized structures having the new framework is of interest. In this manuscript, we report preparation and electron-donating ability of novel azulene-based TTFs (**9-12**), which have a 7-5-5(TTF) condensed ring system.

There are numerous methods to prepare TTF derivatives, and coupling (or cross-coupling) of trithio- and/or dithiocarbonate half-units in the presence of trialkyl phosphite is the most widespread.[7]



Scheme 1

We applied this cross-coupling method to produce azulene-based TTFs. As shown in Scheme 1, azulenodithiocarbonate (**5**), which was prepared by reduction/carbonylation of azulenopentathiepin (**3**),[5] reacted with excess amounts of vinylene trithiocarbonate (**7**) in triethyl phosphite at 110-120 °C for 60 min. The reaction mixture was purified by SiO_2 column chromatography and recrystallization to give azulenotetrathiafulvalene (**9**: Az-TTF, 22% yield) and TTF as a by-product. Yield of TTF could not be determined because of the some instability to SiO_2. 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 ^{1}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 ^{13}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_2Cl_2 appeared at 642 nm (log ε 2.52) as a characteristic peak of *S*-heterocycle-fused azulenes such as azuleno-1,4-dithiin[5] and a 1,2-dithiin with a guaiazulene skeleton.[6] MS spectra gave a molecular ion peak [FAB: *m/z* 304 (M^+)]. 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 ^{1}H NMR and ^{13}C NMR peaks of the ethylenedithio moiety were observed magnetic equivalently at δ3.32 (4H) and δ29.7 (2C), respectively. The other instrumental analysis data also supported the proposed structure.

As for the guaiazulene derivative (**6**),[6] 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)[a] of azulene-based TTFs (**9**-**12**) and azulenes (**1** and **2**)

Compound	$(E_1^{\mathrm{red}})_{\mathrm{pc}}$[b]	$(E_1^{\mathrm{ox}})_{\mathrm{pc}}$[c]	$(E_1^{\mathrm{ox}})_{1/2}$[d]	$(E_1^{\mathrm{ox}})_{\mathrm{pa}}$[e]	$(E_2^{\mathrm{ox}})_{\mathrm{pc}}$[c]	$(E_2^{\mathrm{ox}})_{1/2}$[d]	$(E_2^{\mathrm{ox}})_{\mathrm{pa}}$[e]	$(E_3^{\mathrm{ox}})_{\mathrm{pa}}$[e]
Az-TTF **9**	-1.93	-0.13	-0.04	+0.05	+0.10	+0.22	+0.34	+1.30
Az-(EDT)TTF **10**	-1.92	+0.01	+0.09	+0.17	+0.22	+0.27	+0.33	-
GAz-TTF **11**	-1.34	-0.15	-0.06	+0.04	+0.11	+0.23	+0.35	+1.09
GAZ-(EDT)TTF **12**	-1.46	-0.01	+0.04	+0.09	+0.22	+0.26	+0.31	+1.12
Az **1**	-2.10	-	-	+0.59	-	-	-	-
GAz **2**	-1.24	-	-	+0.40	-	-	-	-

[a] Obtained by cyclic voltammetry: V *vs.* Ag/Ag^+, 10^{-3} M in DMF with 0.1 M Bu_4NClO_4, 100 mV/s. [b] Reduction potentials by the cathodic peak. [c] Oxidation potentials by the cathodic peak. [d] Half-wave oxidation potentials. [e] 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 (Table1). All compounds showed one irreversible wave at reduction region (E_1^{red}) and two or three waves at oxidation region [E_1^{ox}, E_2^{ox}, (E_3^{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 [$(E_1^{ox})_{pa}$/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 [$(E_1^{ox})_{1/2}$/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 [$(E_1^{ox})_{1/2}$/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 CH_2Cl_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 absolutory ionized molecules (e. g., TCNQ; 2227 cm^{-1} and [K][TCNQ]; 2183 cm^{-1} as a CN stretching peak).[10] The IR peak of **13** was shown at 2189 cm^{-1}, and the estimated value was 0.86. The latter afforded black purple solid {**14**, mp 169 °C (dec.), $[\text{GAz-(EDT)TTF}]_2[\text{TCNQ}]_3[CH_2Cl_2]_2$, 2208 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. ^1H and ^{13}C NMR spectra ($SiMe_4$ 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, CH_2Cl_2; ^1H and ^{13}C NMR, $CDCl_3$; MS spectra were taken at fast atom bombardment (FAB) and/or MALDI-TOF method; CV, V *vs.* Ag/Ag$^+$, GC, Pt wire, 0.1 M

Bu_4NClO_4 in DMF. The progress of reactions was followed by TLC method using Merck Silica gel $60F_{254}$.

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_2 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.); ^{1}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); ^{13}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_{max} 642 (2.52), 468 (3.26), 316 (4.24), 225 (4.14); CV (V *vs.* Ag/Ag$^+$) $(E^{red})_{pc}$ -1.93, $(E^{ox})_{pc}$ -0.13, +0.10, $(E^{ox})_{1/2}$ -0.04, +0.22, $(E^{ox})_{pa}$ +0.05, +0.34, +1.30; MS (FAB, NBA) *m/z* 304 (M$^+$). Anal. Calcd for $C_{14}H_8S_4$: 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.); ^{1}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); ^{13}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_{max} 632 (2.91), 469 (3.77), 390 (4.18), 317 (4.69), 280 (4.51); CV (V *vs.* Ag/Ag$^+$) $(E^{red})_{pc}$ -1.92, $(E^{ox})_{pc}$ +0.01, +0.22, $(E^{ox})_{1/2}$ +0.09, +0.27, $(E^{ox})_{pa}$ +0.17, +0.33; MS (MALDI, Dithranol) *m/z* 394 (M$^+$). Anal. Calcd for $C_{16}H_{10}S_6$: C, 48.70; H, 2.55. Found: C, 48.70; H, 2.54.

GAz-TTF (11): dark brown solid; mp 131.5-132 °C; ^{1}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); ^{13}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_{max} 644 (2.95), 459 (3.67), 387 (4.29), 302 (4.68), 237 (4.29); CV (V *vs.* Ag/Ag$^+$) $(E^{red})_{pc}$ -1.34, $(E^{ox})_{pc}$ -0.15, +0.11, $(E^{ox})_{1/2}$ -0.06, +0.23, $(E^{ox})_{pa}$ +0.04, +0.35, +1.09; MS (MALDI, Dithranol) *m/z* 374 (M$^+$). Anal. Calcd for $C_{19}H_{18}S_4$: C, 60.92; H, 4.84. Found: C, 61.18; H, 4.57.

GAz-(EDT)TTF (12): pale green solid; mp 156-157 °C; ^{1}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); ^{13}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_{max} 636 (2.90), 461 (3.72), 383 (4.30), 314 (4.40), 278 (4.38); CV (V *vs.* Ag/Ag$^+$) $(E^{red})_{pc}$ -1.46, $(E^{ox})_{pc}$ -0.01, +0.22, $(E^{ox})_{1/2}$

+0.04, +0.26, $(E^{ox})_{pa}$ +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]$_5$[TCNQ]$_8$): black purple solid; mp 165 °C (dec.); IR *ν* 4000 (br), 2189. Anal. Calcd for [GAz-TTF]$_5$[TCNQ]$_8$ ($C_{191}H_{122}N_{32}S_{20}$): 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]$_2$[TCNQ]$_3$[CH$_2$Cl$_2$]$_2$): black green solid; mp 169 °C (dec.); IR *ν* 5000-4000 (br), 2208. Anal. Calcd for [GAz-(EDT)TTF]$_2$[TCNQ]$_3$[CH$_2$Cl$_2$]$_2$ ($C_{80}H_{56}Cl_4N_{12}S_{12}$): C, 56.13; H, 3.30; N, 9.82. Found: C, 56.80; H, 2.95; N, 9.87.

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