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Synthesis and Properties of New Donors. 1,6-Methano[10]annulene and Naphthalene Derivatives with Tetrathiafulvalene Substituents

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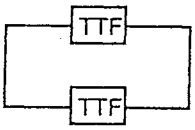
New donors, containing one or two tetrathiafulvalenes at 2-, 2,7- and 2,10-positions of 1,6-methano[10]annulene or at 1,8-positions of naphthalene, have been synthesized. Through-space and/or through-bond interactions between TTF units in these compounds have been investigated by means of cyclic voltammetry.

Many derivatives of tetrathiafulvalene (TTF) are well-known, because their CT-complexes or radical-cation salts are organic metals that display conductivity or even superconductivity at low temperatures.[1] We are especially interested in the interactions of face-to-face fixed TTF moieties. The cyclophanes **1** containing two TTF units have been synthesized and through-space interaction between spacially close TTF moieties has been investigated.[2] However, TTF moieties incorporated in the cyclophane framework are usually forced to take a bent conformation, showing some effects of bending. If two TTF units are introduced to the peri-position of 1,8-methano[10]annulene or naphthalene like **2** and **3**, through-space and/or through-bond interactions between planar TTF units can be expected. We report here the synthesis and properties of novel donors (**2** and **3**) and related compounds.



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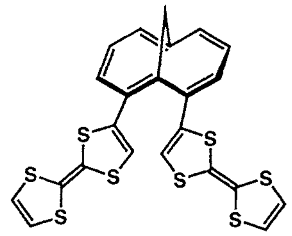

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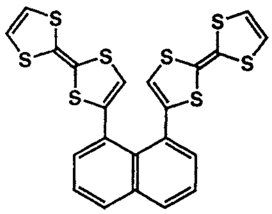

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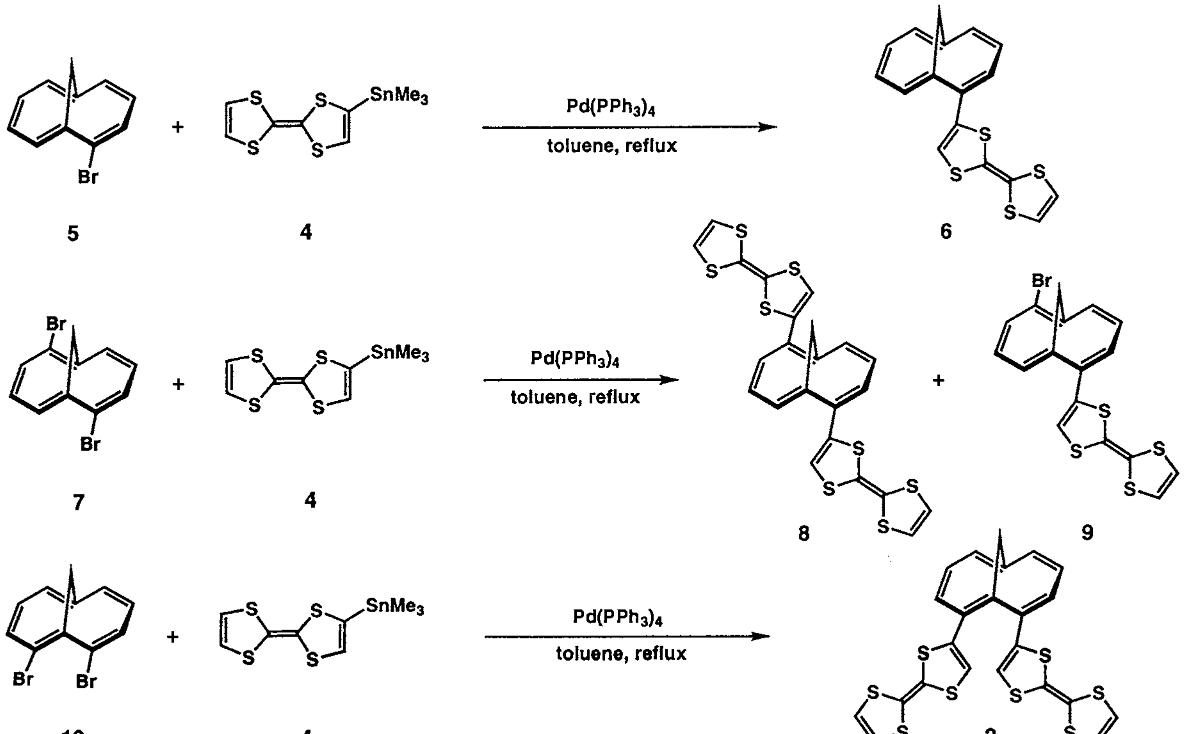
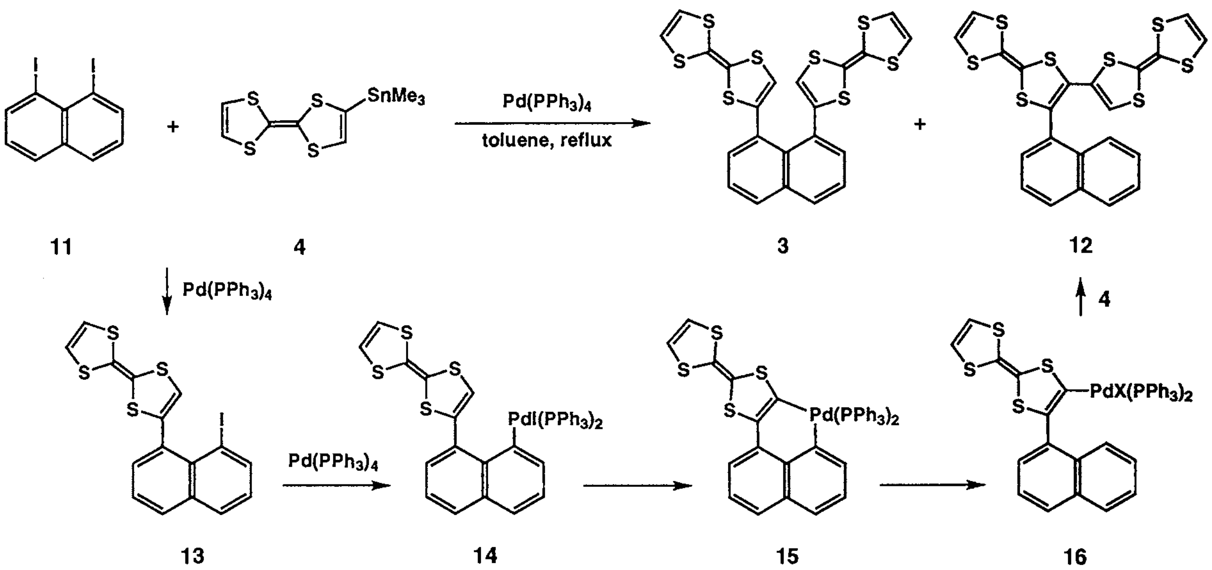
For the synthesis of **2**, **3**, and related compounds, we applied the palladium-catalyzed cross-coupling reaction of halogenated arenes with (trimethylstannyl)tetrathiafulvalene **4**.[3] As shown in Scheme 1, Pd(PPh$_3$)$_4$ (10 mol%) was added to a solution of 2-bromo-1,6-methano[10]annulene (**5**)[4] and **4** in toluene, and the mixture was refluxed for 3.5 h under nitrogen. The product was separated by column chromatography on deactivated alumina, followed by purification using gel-permeation chromatography to give **6** in 33% yield.[5] In a similar manner, the reaction of 2,7-dibromo-1,6-methano[10]annulene (**7**)[6] with **4** in the presence of Pd(PPh$_3$)$_4$ (20 mol%) produced 2,7-bis(tetrathiafulvalenyl)-1,6-methano[10]annulene (**8**) in 19% yield together with the mono-substituted product (**9**, 11%). Interestingly, the reaction of sterically hindered **10**[6] with **4** in the presence of Pd(PPh$_3$)$_4$ (20 mol%) in refluxing toluene proceeded smoothly to afford the desired di-substituted product **2** in 21% yield.



Scheme 1.

As shown in Scheme 2, a similar reaction of 1,8-diiodonaphthalene (**11**) with **4** in the presence of Pd(PPh$_3$)$_4$ gave 1,8-bis(tetrathiafulvalenyl)naphthalene (**3**) in 14% yield, together with the rearranged product (**12**, 5%). The formation of **12** can be explained by considering the cyclization of the intermediate **14**, followed by cleavage of the palladium-naphthalene bond (Scheme 2). The resulting **16** reacts with **4** in a usual way to give **12**.



Scheme 2.

All new donors reported here are red or orange-red crystalline solids which decompose gradually at room temperature. The examination of the NMR data exhibited no suggestions for any interaction between the "parallel" TTF moieties. In ^{1}H NMR spectra one TTF proton near aromatic rings in **2** and **3** shows an upper field shift of 0.45 ppm as compared with the same proton in **8**. This upper field shift may be attributable to the shielding effect from the neighboring TTF moiety. Although 1,8-diarylnaphthalenes show the temperature-dependent ^{1}H NMR spectra due to restricted rotation of aryl moieties,[7)] the ^{1}H NMR spectra of **2** and **3** at room temperature suggest a rather fast rotation of TTF units.

In order to estimate the interactions between two TTF moieties, redox potentials of new donors were measured by cyclic voltammetry (CV). As shown in Table 1, the potentials of **6**, **8**, and **9** show, as expected, similar values for the first and second oxidations as unsbstituted TTF does, whereas the compounds **2** and **3** reveal a significantly different redox-behavior. The first half-wave potentials in **2** and **3** are 0.06-0.07 V lower than those of TTF. On the other hand, the second half-wave potentials are 0.15-0.17 V higher. These observations result in a bigger difference between the first and second half-wave potentials ($\Delta E_{1/2}$) as compared with the $\Delta E_{1/2}$-values of TTF, **6**, **8**, and **9**. The cyclic voltammogram of **2**, as well as **3**, displays no splitting for each redox peak, indicating the occurrence of two-electron redox-process at one step in each case. This behavior proves interaction between the TTF units in **2** and **3** as follows. The first oxidation, which leads to bis(radical-cation) species, is accelerated by closely situated TTF units within the sum of van der Waals radii,[8,9)] because the radical-cation species can interact with shorter C•••C and S•••S contacts.[10)] However, the second oxidation is restrained by this stabilizing interaction and repulsion of positive charges, which makes it more difficult to generate the tetracation species.

It is known that 1,8-ferrocenylnaphthalene shows two one-electron oxidations ($\Delta E_{1/2}$ = 0.15 V in CH_3CN).[11)] However, **2** and **3** show no separation of the first oxidation step, although the interaction between two TTF units makes the first potential lower. The interactions of the TTF units in **2** and **3** may be a combined effect of through-space and through-bond interactions, in which through-space interaction occupies a major part.

The new donor molecules reported here gave CT-complexes with tetracyano-*p*-quinodimethane (TCNQ). The measurement of conductivity of the CT-complexes and radical-cation salts is now under investigation.

Table 1. Cyclic voltammetric data[a)] for **6**, **8**, **9**, **2**, and **3**

Compound	$E^1_{1/2}$/V [$E_{pa} - E_{pc}$/mV]	$E^2_{1/2}$/V [$E_{pa} - E_{pc}$/mV]	$\Delta E_{1/2}$ ($E^2_{1/2} - E^1_{1/2}$)
TTF	0.36 [165]	0.74 [210]	0.38
6	0.39 [135]	0.78 [135]	0.39
8	0.40 [145]	0.79 [210]	0.39
9	0.40 [130]	0.73 [130]	0.33
2	0.29 [155]	0.89 [120]	0.60
3	0.30 [190]	0.91 [200]	0.61

[a] Experimental Conditions: n-Bu_4NClO_4 (0.1 mol dm^{-3}) in dry benzonitrile at room temperature; Pt working and counter electrodes. Potentials were measured against a Ag/Ag$^+$ electrode and converted to the value vs SCE (Fc/Fc$^+$) = 0.31 V.

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5) The structures of all new compounds reported here were fully characterized by the spectroscopic analysis. The selected data are as follows. **6**: EI-MS (*m/z*) 344 (M^+); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (m, 1H), 7.40 (m, 2H), 7.22 (m, 1H), 7.14 (m, 2H), 6.96 (m, 1H), 6.59 (s, 1H), 6.29 (s, 2H), -0.17 (d, J = 9.3 Hz, 1H), -0.50 (d, J = 9.3, 1H). **8**: FAB-MS (*m/z*) 546 (M^+); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.8, 2H), 7.25 (d, J = 9.8, 2H), 7.08 (dd, J = 9.8, 8.8, 2H), 6.49 (s, 2H), 6.29 (s, 4H), -0.24 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.19, 132.66, 130.08, 127.85, 127.69, 119.15, 118.98, 118.45, 117.08, 111.50, 109.69, 35.28. **9**: EI-MS (*m/z*) 422, 424 (M^+); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (m, 1H), 7.70 (m, 1H), 7.40 (m, 1H), 7.24 (m, 1H), 7.09 (m, 2H), 6.60 (s, 1H), 6.34 (s, 2H), -0.14 (d, J = 9.3, 1H), -0.32 (d, J = 9.3, 1H). **2**: FAB-MS (*m/z*) 546 (M^+); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.8, 2H), 7.25 (d, J = 9.8, 2H), 7.15 (dd, J = 9.8, 8.8, 2H), 6.29 (AB q, J = 6.4, $\Delta\nu_{AB}$ = 5.3 Hz, 4H), 6.05 (s, 2H), -0.25 (s, 2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.61, 132.33, 129.97, 129.72, 127.27, 121.18, 118.98, 118.85, 118.07, 112.98, 111.23, 110.39, 35.79. **3**: FAB-MS (*m/z*) 532 (M^+); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, J = 8.3, 1.0, 2H), 7.59 (dd, J = 6.8, 1.0, 2H), 7.45 (dd, J = 8.3, 6.8, 2H), 6.29 (AB q, J = 6.6, $\Delta\nu_{AB}$ = 8.2, 4H), 6.04 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.19, 133.48, 130.78, 130.23, 129.75, 125.38 (10 carbons of naphthalene part), 119.09, 118.80, 118.05 (8 carbons of S-C=C-S in TTF parts), 111.06, 110.59 (4 central carbons of TTF parts). **4**: FAB-MS (*m/z*) 532 (M^+); ^{1}H NMR ($CDCl_3$) δ 7.97 (m, 1H), 7.92 (m, 1H), 7.87 (m, 1H), 7.50 (m, 4H), 6.33 (AB q, J = 6.4, $\Delta\nu_{AB}$ = 9.3, 2H), 6.15 (AB q, J = 6.2, $\Delta\nu_{AB}$ = 13.2, 2H), 6.08 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 133.50, 132.39, 130.96, 130.49, 129.24, 128.44, 127.21, 126.52, 125.20 x 2 (10 carbons of naphthalene part), 128.29, 126.39, 123.19, 120.43, 119.20, 119.07, 118.96, 118.62 (8 carbons of S-C=C-S in TTF parts), 113.51, 111.94, 109.07, 106.27 (4 central carbons of TTF parts).

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