

SYNTHESIS OF NEW WEITZ TYPE π -DONORS AND FORMATION OF CHARGE
TRANSFER COMPLEXES

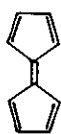
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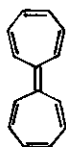
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Abstract — Several iso- π -electronic thia-heteroanalogues of heptafulvalene were synthesized by Wittig-Horner reaction of the corresponding tropones with 2-diethoxyphosphinyl-1,3-benzodithiole. Some of them reacted with π -acceptors such as TCNQ or DDQ in hot MeCN to give new stable charge transfer complexes.

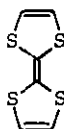
Fulvalene (1) and heptafulvalene (2), typical cross conjugated carbocyclic unsaturated compounds, have been of interest in connection with synthetical and theoretical fields and have been extensively investigated¹. In recent years tetrathiafulvalene (TTF)², 4,4'-bithiopyranylidene (BTP)³, and their derivatives, which are stable iso- π -electronic heteroanalogues of 2, were reported as Weitz type π -donors and a lot of electrically conductive charge transfer complexes with electron acceptors such as 7,7,8,8-tetracyanoquinodimethane (TCNQ) or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were synthesized⁴. Heteroheptafulvalenes (3, 4) containing heteroatoms in one ring of 2 were also reported⁵. However this type of π -donors did not give charge transfer complexes.



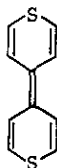
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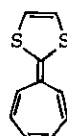
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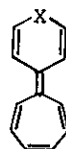
TTF



BTP



3

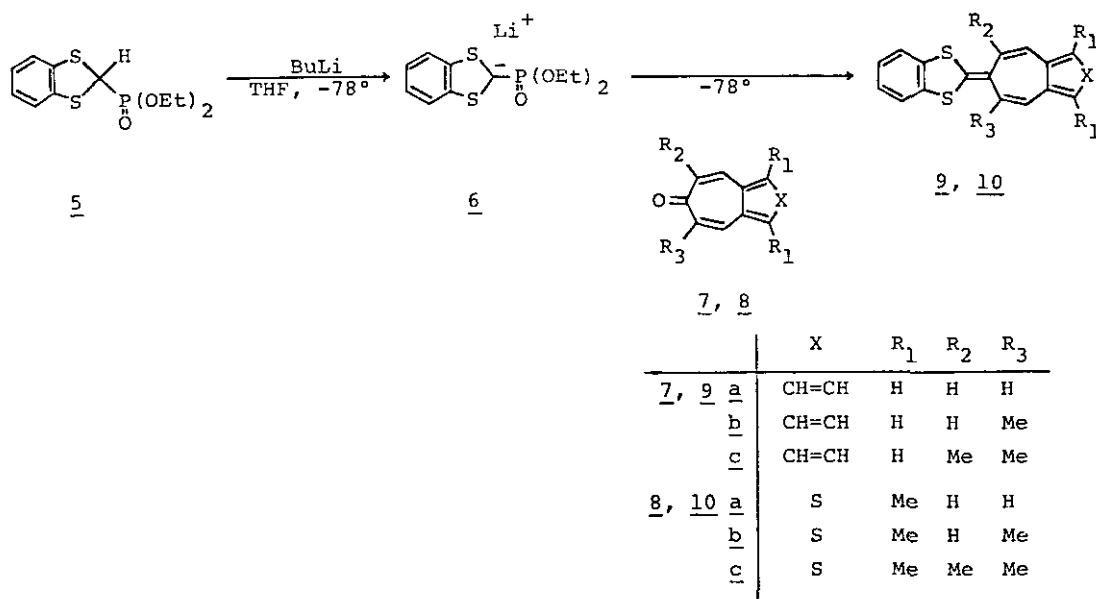


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X = O, S

In this paper we wish to report the synthesis and properties of new Weitz type π -donors belonging to the type 3 and their reactivities with π -acceptors. Heteroheptafulvalenes were synthesized as shown in Scheme 1. 2-Diethoxyphos-

Scheme 1



phenyl-1,3-benzodithiophene (5)⁶ was deprotonated with butyllithium in tetrahydrofuran (THF) at -78°C and the resulted phosphonate carbanion (6) was allowed to react with substituted 4,5-benzotropones (7a-c)⁷ and 2-thiaazulen-6-ones (8a-c)⁸ to give the corresponding 2-(7H-benzocyclohepten-7-ylidene)-1,3-benzodithiophenes (9a-c) and 2-(2-thiaazulen-6-ylidene)-1,3-benzodithiophenes (10a-c) in good yields, respectively, as shown in Table 1. The structures of 9 and 10 were confirmed by

Table 1 Yields and Physicochemical Data of 9 and 10

No.	Appearance (recryst. solv.)	Yield (%)	mp (°C)
<u>9a</u>	red plates (EtOAc)	85	261-262
<u>9b</u>	yellow needles (EtOAc)	72	235-236
<u>9c</u>	colorless prisms (EtOAc)	75	221-223
<u>10a</u>	yellow needles (MeCN)	84	224-226
<u>10b</u>	yellow prisms (MeCN)	74	149-151
<u>10c</u>	colorless prisms (MeCN)	85	217-218

means of the elemental analysis, IR, $^1\text{H-NMR}$, UV, and mass spectra. UV spectra of 9 and 10 are shown in Figs 1 and 2, respectively.

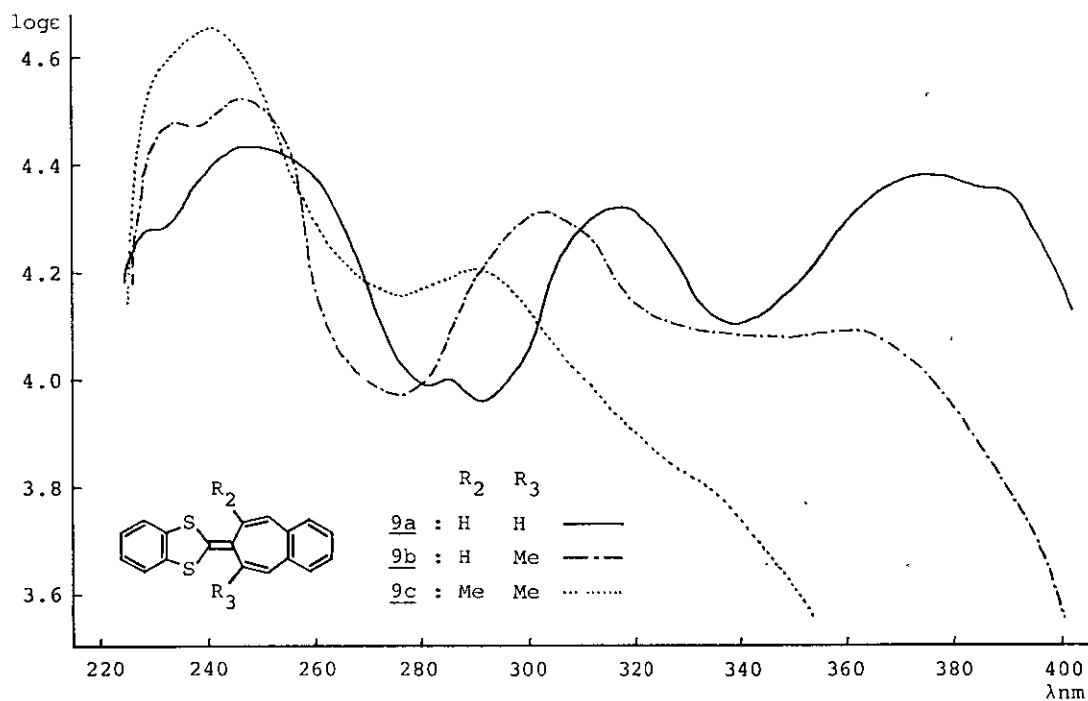


Fig. 1 UV Spectra of 9 in MeCN

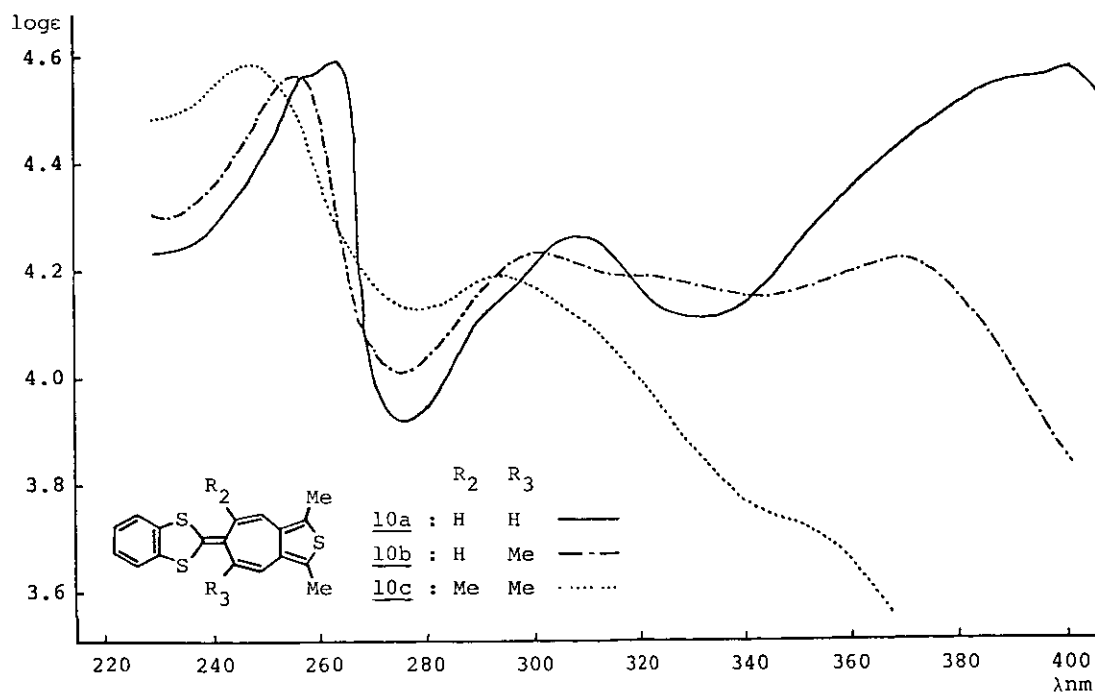


Fig. 2 UV Spectra of 10 in MeCN

Each of the absorption maxima of 9b,c and 10b,c showed hypsochromic shifts compared with those of 9a and 10a, and the absorbances of 9b,c and 10b,c were diminished. These observations show the steric hindrance between the sulfur atoms in dithiole ring and the methyl groups of cycloheptatriene ring contributes to diminish the coplanarity of heteroheptafulvalenes (9b,c and 10b,c). Charge transfer complex formation of these heteroheptafulvalenes with several π -acceptors was examined and the results were shown in Table 2.

Scheme 2

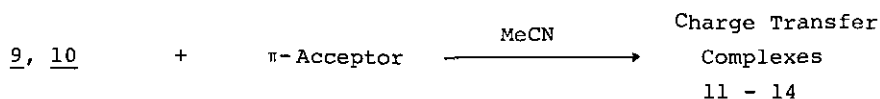


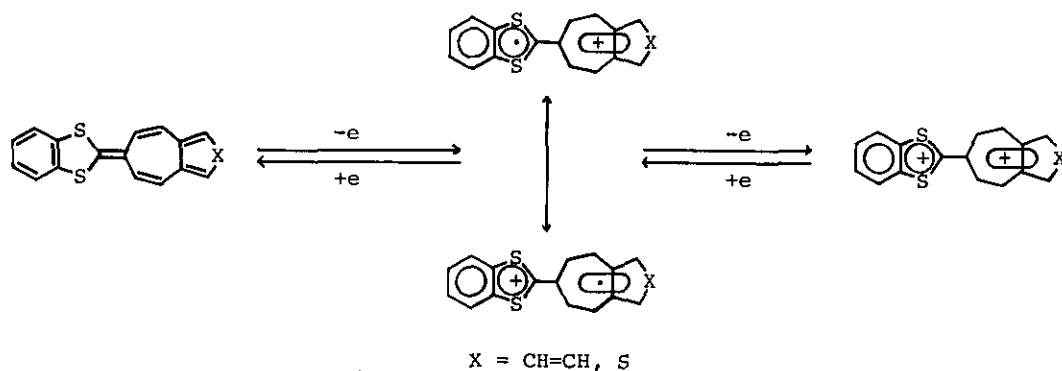
Table 2 Charge Transfer Complexes of 9 and 10

π -Donor \ π -Acceptor	DDQ	TCNQ
<u>9a</u>	C.T.Complex (<u>11a</u>) purple-black powder	C.T.Complex (<u>12a</u>) purple-black powder
<u>9b</u>	(C.T.Complex) (<u>11b</u>) brown powder	no reaction
<u>9c</u>	(C.T.Complex) (<u>11c</u>) brown powder	no reaction
<u>10a</u>	C.T.Complex (<u>13a</u>) purple-black powder	C.T.Complex (<u>14a</u>) purple-black powder
<u>10b</u>	(C.T.Complex) (<u>13b</u>) brown powder	no reaction
<u>10c</u>	(C.T.Complex) (<u>13c</u>) brown powder	no reaction

Compounds 9a and 10a reacted with an equimolecular amount of DDQ or TCNQ in hot MeCN to give purple-black crystalline powders. These products were recognized to be charge transfer complexes by the following data. Elemental analysis showed 11a - 14a are simple salts (1:1 charge transfer complex). In the IR spectra 12a and 14a had the CN stretching band at 2200 cm^{-1} whereas TCNQ itself has that band⁹ at 2220 cm^{-1} . Similarly 11a and 13a had the CN stretching band at 2200 cm^{-1} whereas DDQ itself has that at 2235 cm^{-1} . Furthermore C=O stretching band at

1661 cm^{-1} of DDQ was absent in the charge transfer complexes (11a, 13a), instead at 1570 cm^{-1} phenoxy radical band appeared¹⁰. Compounds 9b,c and 10b,c also reacted with DDQ in MeCN to precipitate purple-black crystalline powders, which were probably charge transfer complexes, but they are too air-sensitive to isolate and decomposed to brown powders. On the other hand, these fulvalenes 9b,c and 10b,c did not react with TCNQ, and no precipitation formed. Furthermore these compounds 9 and 10 did not react with TCNE in contrast to 2, 3, and 4 containing cycloheptatriene ring which reacted with TCNE to give 1:1 adducts^{5,11}. These results indicate 9a and 10a are stronger π -donors than 9b,c and 10b,c which have methyl groups at cycloheptatriene ring. Considering methyl groups of 9b,c and 10b,c as electron donating groups, these results seem to be conflicting, but we consider the steric effects between the methyl groups in cycloheptatriene ring and the sulfur atoms in dithiole ring play stronger role in forming charge transfer complexes than the electronic effect of methyl groups. Namely as steric repulsion between the methyl groups and the sulfur atoms decreases the coplanarity of 9b,c and 10b,c, these compounds could not get sufficient delocalization energy by forming new aromatic ring which are resulted by one electron oxidation of heteroheptafulvalenes (Scheme 3). The room temperature resistivities of charge transfer complexes (11 - 14) are summarized in Table 4. DDQ is superior to TCNE as an acceptor, and this finding is in agreement with the result of Ueno et al.¹² Resistivities of the charge complexes, 13a and 14a were lower than those of 11a and 12a. This would be attributed to the lower oxidation-reduction potential of 2-thiaazulene moiety than that of benzocycloheptene.

Scheme 3



EXPERIMENTAL

Melting points were taken on a Yanagimoto micro-melting point apparatus and are uncorrected. Microanalyses were performed at the Microanalytical Laboratory of our college. Nuclear magnetic resonance spectra were recorded on a Hitachi R-20B spectrometer and chemical shifts are given in parts per million relative to trimethylsilane as an internal standard. Infrared spectra were obtained from a JASCO Model IRA-1. Ultra violet spectra were determined on a Hitachi 200-10. The EI mass spectra were taken on a JEOL JMS-D 300 spectrometer.

Synthesis of 2-(7H-benzocyclohepten-7-ylidene)-1,3-benzodithioles (9a-c) and 2-(2-thiaazulen-6-ylidene)-1,3-benzodithioles (10a-c)

General procedure: To a solution of phosphonate (5, 2.0 mmol) in THF (20 ml) was added butyllithium in ether (2.0 ml, 2.2 mmol) at -78°C under nitrogen with stirring. 4,5-Benzotropones (7a-c) or 2-thiaazulen-6-ones (8a-c) were added to a

Table 3 Analytical and Spectral Data of 9 and 10

No.	MS m/e	Formula	Analysis		C	H	NMR (CDCl ₃)	δ
			Calcd.	Found				
<u>9a</u>	292 (M ⁺)	C ₁₈ H ₁₂ S ₂	73.94	4.14	73.99	4.02	(a)	
<u>9b</u>	306 (M ⁺)	C ₁₉ H ₁₄ S ₂	74.47	4.60	74.48	4.52	(a)	
<u>9c</u>	320 (M ⁺)	C ₂₀ H ₁₆ S ₂	74.96	5.03	75.13	4.89	2.21 (6H, d, J=1.3Hz, CH ₃) 6.53 (2H, q, J=1.3Hz, C ₂ , C ₄ , -H) 6.85 (8H, m, Ar-H)	
<u>10a</u>	326 (M ⁺)	C ₁₈ H ₁₄ S ₃	66.22	4.32	66.21	4.09	(a)	
<u>10b</u>	340 (M ⁺)	C ₁₉ H ₁₆ S ₃	67.02	4.74	66.92	4.70	2.23 (3H, d, J=1.5Hz, C ₅ , -CH ₃) 2.34 (6H, s, C ₁ , C ₃ , -CH ₃) 5.92 (1H, d, J=10Hz, C ₇ , -H) 6.27 (1H, q, J=1.5Hz, C ₄ , -H) 6.38 (1H, d, J=10Hz, C ₈ , -H) 6.90-7.36 (4H, m, Ar-H)	
<u>10c</u>	354 (M ⁺)	C ₂₀ H ₁₈ S ₃	67.75	5.12	67.95	4.96	2.15 (6H, d, J=1.5Hz, C ₅ , C ₇ , -CH ₃) 2.34 (6H, s, C ₁ , C ₃ , -CH ₃) 6.32 (2H, q, J=1.5Hz, C ₄ , C ₈ , -H) 6.85-7.20 (4H, m, Ar-H)	

a) Insoluble in ordinary solvents.

solution of 6 after 10 min. The mixture was stirred for 1 h at -78°C and then allowed to get warm to room temperature. THF was evaporated under reduced pressure, and the residue was extracted with CH_2Cl_2 after addition of water. The extracts were dried over anhydrous magnesium sulfate and evaporated to dryness under reduced pressure. The residual solid was recrystallized from an appropriate solvent to give the corresponding heteroheptafulvalenes 9 or 10. Elemental analysis and spectral data are shown in Table 3.

Formation of charge transfer complexes

General procedure: A suspension of 9a or 10a (1.0 mmol) and TCNQ or DDQ (1.0 mmol) in MeCN (30 ml) was refluxed under nitrogen for 20 min and then allowed to cool to room temperature. Charge transfer complexes (11a - 14a) formed were collected by filtration and air-dried. Yields, mp, and elemental analysis are shown in Tables 4 and 5.

Table 4 Yields, Physicochemical Data and Resistivity of 11 - 14

No.	Yield (%)	mp ($^{\circ}\text{C}$)	IR (cm^{-1})	ρ ($\Omega \text{ cm}$) ^{a)}
<u>11a</u>	82	208-210	2200	3.6×10^5
<u>12a</u>	83	198-201	2200 1570	1.5×10^7
<u>13a</u>	92	300<	2200	1.0×10^2
<u>14a</u>	86	227-230	2200 1570	9.4×10^6

a) Measured on compressed pellets at room temperature.

Table 5 Mass Spectral and Analytical Data of 11 - 14

No.	Formula	MS m/e	Analysis					
			Calcd.			Found		
			C	H	N	C	H	N
<u>11a</u>	$\text{C}_{26}\text{H}_{12}\text{Cl}_2\text{N}_2\text{O}_2\text{S}_2$	292, 228	60.12	2.33	5.39	60.17	2.27	5.38
<u>12a</u>	$\text{C}_{30}\text{H}_{16}\text{N}_4\text{S}_2$	292, 204	72.56	3.25	11.28	72.84	3.07	11.33
<u>13a</u>	$\text{C}_{26}\text{H}_{14}\text{Cl}_2\text{N}_2\text{O}_2\text{S}_3$	326, 228	56.42	2.55	5.06	56.46	2.50	5.33
<u>14a</u>	$\text{C}_{30}\text{H}_{18}\text{N}_4\text{S}_3$	326, 204	67.90	3.42	10.56	67.98	3.31	10.50

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