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

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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-benzodi-
thiole. 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 unsatu-
rated compounds, have been of interest in connection with synthetical and theoret-
ical fields and have been extensively investigated[1]. In recent years tetrathia-
fulvalene (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-di-
cyano-1,4-benzoquinone (DDQ) were synthesized[4]. Heteroheptafulvalenes (3,4) con-
taining heteroatoms in one ring of 2 were also reported[5]. However this type of
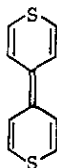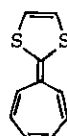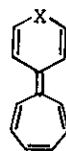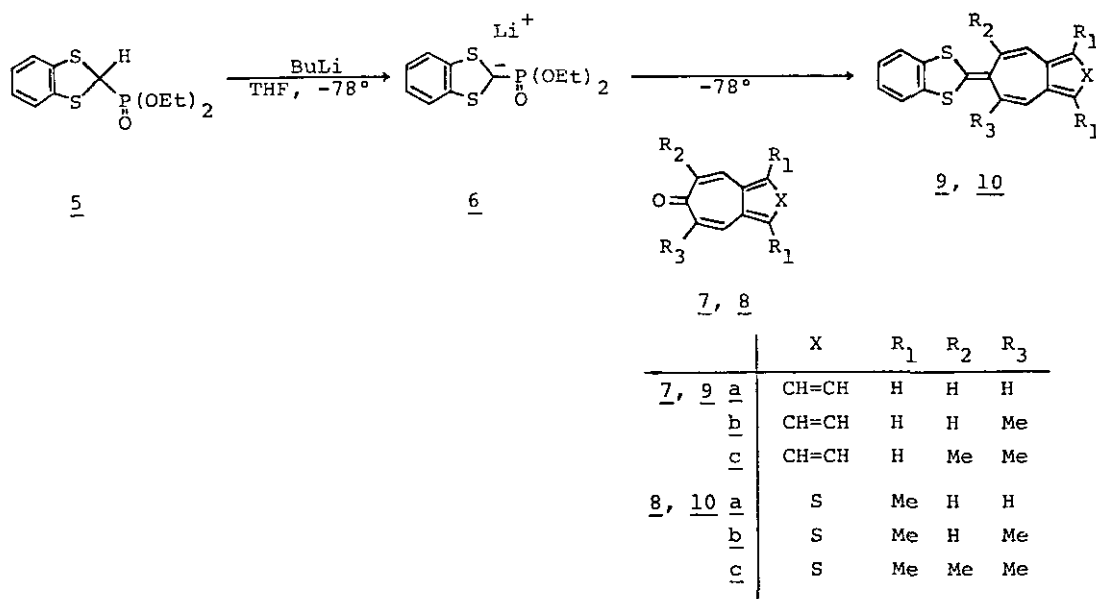π-donors did not give charge transfer complexes.
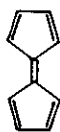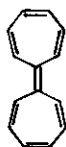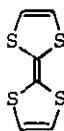
| 1 | 2 | TTF | BTP | 3 | 4 |

X = O, S

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

<div align="center">Scheme 1</div>

	X	R_1	R_2	R_3
$\underline{7}$, $\underline{9}$ $\underline{a}$	CH=CH	H	H	H
$\underline{b}$	CH=CH	H	H	Me
$\underline{c}$	CH=CH	H	Me	Me
$\underline{8}$, $\underline{10}$ $\underline{a}$	S	Me	H	H
$\underline{b}$	S	Me	H	Me
$\underline{c}$	S	Me	Me	Me

phinyl-1,3-benzodithiole ($\underline{5}$)[6] was deprotonated with butyllithium in tetrahydro-furan (THF) at -78°C and the resulted phosphonate carbanion ($\underline{6}$) was allowed to react with substituted 4,5-benzotropones ($\underline{7a-c}$)[7] and 2-thiaazulen-6-ones (8a-c)[8] to give the corresponding 2-(7H-benzocyclohepten-7-ylidene)-1,3-benzodithioles ($\underline{9a-c}$) and 2-(2-thiaazulen-6-ylidene)-1,3-benzodithioles ($\underline{10a-c}$) in good yields, respectively, as shown in Table 1. The structures of $\underline{9}$ and $\underline{10}$ were confirmed by

<div align="center">Table 1 Yields and Physicochemical Data of $\underline{9}$ and $\underline{10}$</div>

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

means of the elemental analysis, IR, ^{1}H-NMR, UV, and mass spectra. UV spectra of

9 and 10 are shown in Fig.s 1 and 2, respectively.

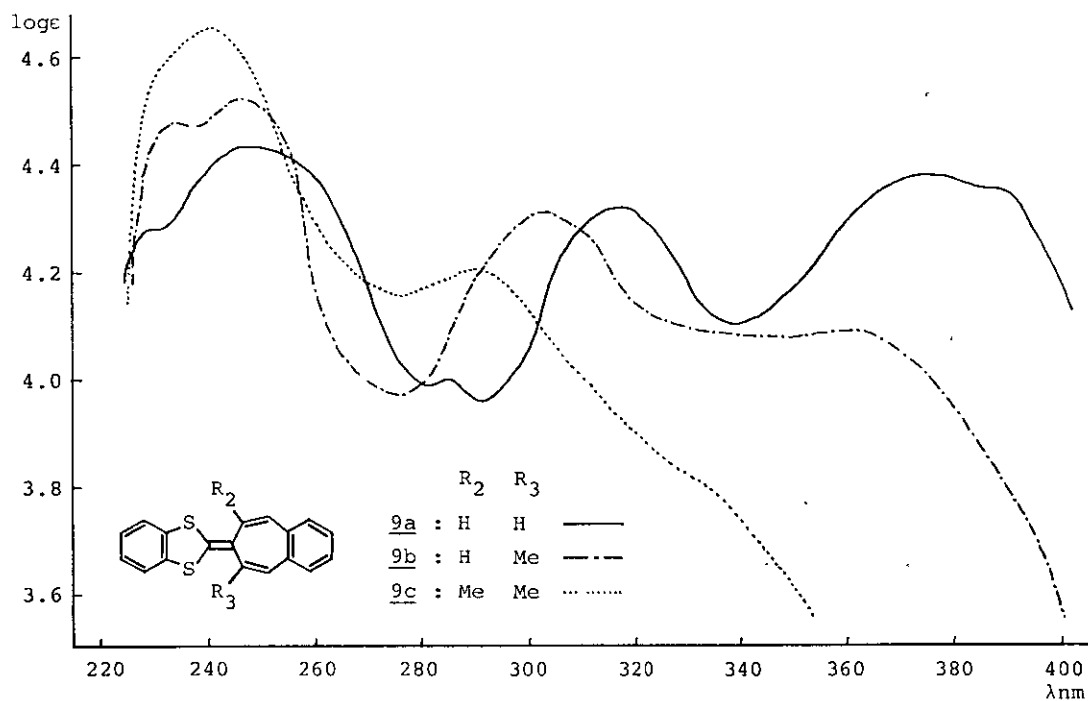|	R$_2$	R$_3$
9a :	H	H
9b :	H	Me
9c :	Me	Me

Fig. 1   UV Spectra of 9 in MeCN

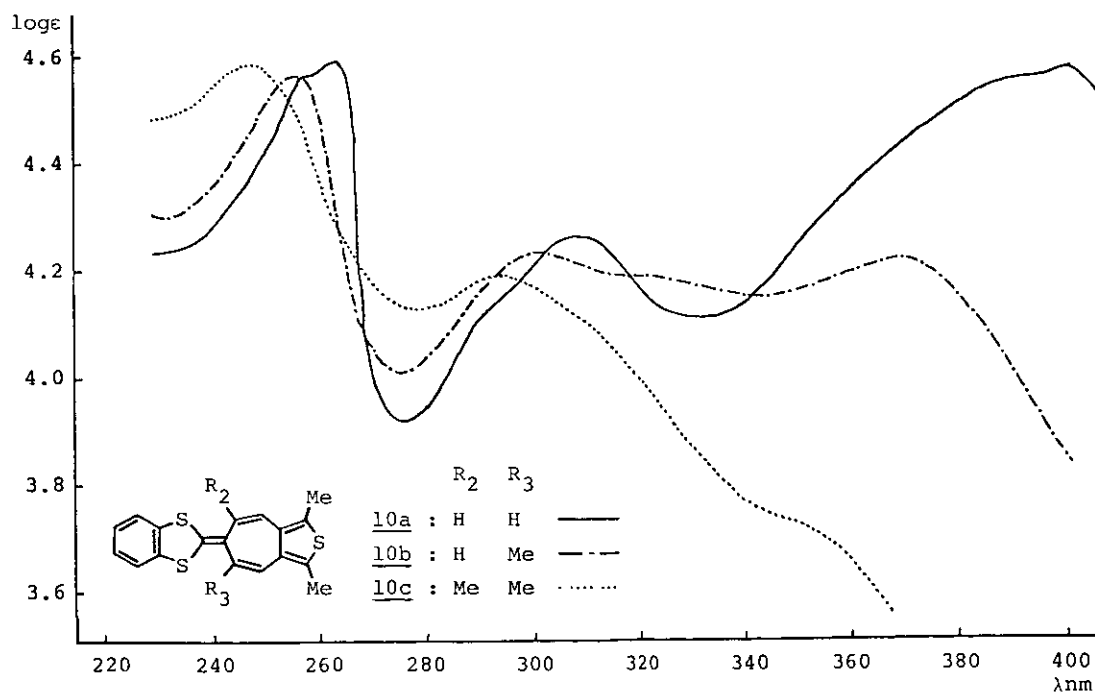|	R$_2$	R$_3$
10a :	H	H
10b :	H	Me
10c :	Me	Me

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.
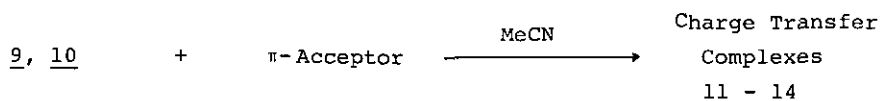
Scheme 2

9, 10   +   π-Acceptor $\xrightarrow{\text{MeCN}}$ Charge Transfer Complexes 11 - 14

Table 2 Charge Transfer Complexes of 9 and 10

π-Donor \ π-Acceptor	DDQ	TCNQ
9a	C.T.Complex (11a) purple-black powder	C.T.Complex (12a) purple-black powder
9b	(C.T.Complex) (11b) brown powder	no reaction
9c	(C.T.Complex) (11c) brown powder	no reaction
10a	C.T.Complex (13a) purple-black powder	C.T.Complex (14a) purple-black powder
10b	(C.T.Complex) (13b) brown powder	no reaction
10c	(C.T.Complex) (13c) 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 band[9] 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 appeared[10]. 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 delocarization energy by
forming new aromatic ring which are resulted by one electron oxidation of hetero-
heptafulvalenes (Scheme 3). The room temperature resistivities of charge transfer
complexes (11 - 14) are summerized 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

X = CH=CH, S
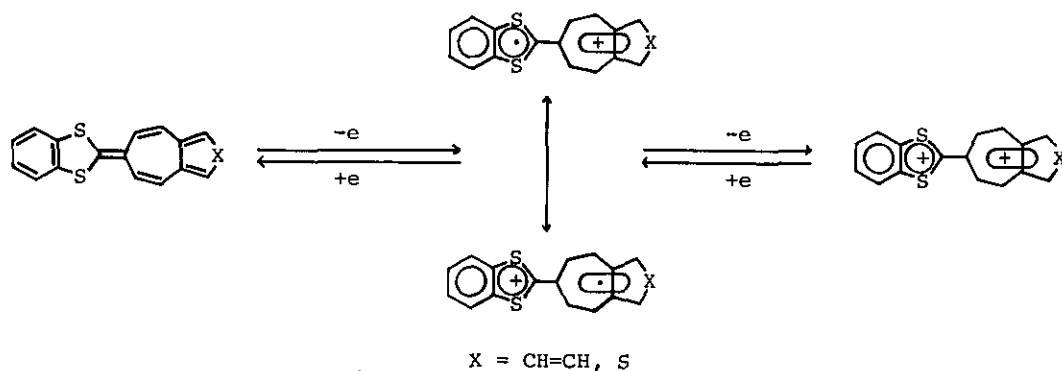
EXPERIMENTAL

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 milliom relative to tri-methylsilane 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 stir-ring. 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				NMR (CDCl$_3$) ·δ
			Calcd.		Found		
			C	H	C	H	
9a	292(M$^+$)	C$_{18}$H$_{12}$S$_2$	73.94	4.14	73.99	4.02	(a)
9b	306(M$^+$)	C$_{19}$H$_{14}$S$_2$	74.47	4.60	74.48	4.52	(a)
9c	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)
10a	326(M$^+$)	C$_{18}$H$_{14}$S$_3$	66.22	4.32	66.21	4.09	(a)
10b	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)
10c	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 (°C)	IR (cm^{-1})		ρ (Ω cm)[a]
11a	82	208-210	2200		3.6×10^5
12a	83	198-201	2200	1570	1.5×10^7
13a	92	300<	2200		1.0×10^2
14a	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	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
11a	$C_{26}H_{12}Cl_2N_2O_2S_2$	292, 228	60.12	2.33	5.39	60.17	2.27	5.38
12a	$C_{30}H_{16}N_4S_2$	292, 204	72.56	3.25	11.28	72.84	3.07	11.33
13a	$C_{26}H_{14}Cl_2N_2O_2S_3$	326, 228	56.42	2.55	5.06	56.46	2.50	5.33
14a	$C_{30}H_{18}N_4S_3$	326, 204	67.90	3.42	10.56	67.98	3.31	10.50

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