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CONVERSION OF TETRABENZOBIS(THIOPYRANYLIDENE)ETHENE TO A NEW DONOR CONTAINING A PENTALENE SKELETON, DIBENZODITHIAACENAPHTHACENAPHTHYLENE, AND THEIR CHARGE TRANSFER COMPLEXES

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Dibenzodithiaacenaphthacenaphthylene was prepared from benzobis(thiopyranylidene)ethene. Both compounds are good electron donors and gave CT complexes with TCNQ, $TCNQF_4$, and DDQ. The DDQ complexes represent the rare examples of CT complexes with relatively low resistivities despite having neither TTF-type donor nor TCNQ-type acceptor.

We have recently reported a series of new Weitz-type donors having a cumulenic bond such as tetraphenyl and tetrabenzo derivatives of 1,2-bis(4H-thiopyran-4-ylidene)ethene (BTPE,**1**).1-3) In view of the fact that a highly amphoteric condensed hydrocarbon, pentaleno[1,2,3-cd;4,5,6-c'd']diphenalene (PDPL,**2**),4) has been prepared by treatment of 1,2-bis(phenalen-1-ylidene)ethane5) or ethene (BPLE,**3**)6) with molten salt comprising $AlCl_3$ and NaCl, tetrabenzo-BTPE (Bz_4BTPE,**4**)1) would be a potential candidate to construct a new sulfur heterocycle containing a condensed pentalene moiety. In this paper we present a successful conversion of Bz_4BTPE **4** into dibenzo[ak]-3,9-dithiaacenaphthacenaphthylene (Bz_2DTAA,**5**) by the molten salt dehydrocyclization technique. Since both the starting material **4** and the product **5** of this reaction appeared to be good electron donors, we have also studied some charge-transfer (CT) complexes derived from **4** and **5**.

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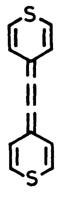
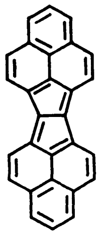
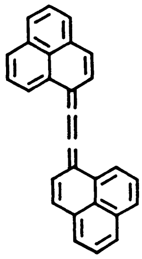
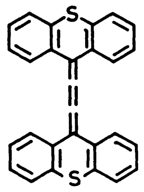
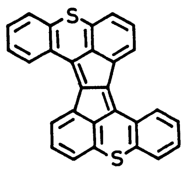
Bz$_2$DTAA **5** was obtained simply by treatment of **4** with $AlCl_3$-NaCl at elevated temperature.[7)] Elemental analysis and MS[8)] of **5** indicate the loss of two hydrogen atoms from **4**. The structure of **5** was assigned primarily on the basis of its ^{1}H NMR spectrum[8)] which shows the signals responsible for an AMX and an ABCX systems. In the electronic spectrum of **5**,[8)] a broad and strong absorption band is observed in the longest wavelength region. The absorption maximum of **5** shows a substantial red shift by 74 nm compared with that of **4**.[1)]

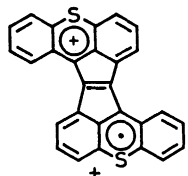

BTPE, 1

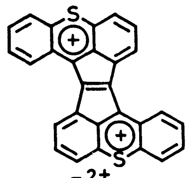

PDPL, 2

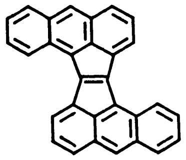

BPLE, 3


Bz$_4$BTPE, 4


Bz$_2$DTAA, 5


$5^{+\cdot}$


5^{2+}


6

Here we would like to point out the structural feature of Bz$_2$DTAA **5** as a peri-condensed Weitz-type donor,[9)] the corresponding carbon skeleton of which is dibenzo[ak]acenaphthacenaphthylene (**6**). Thus replacement of two of the sp^2 carbon atoms in **6** by two sulfur atoms produces **5**. Such a structural feature may contribute to stabilize the oxidized cationic forms and thereby bestow the donor ability, since the cation radical and the dication forms ($5^{+\cdot}$ and 5^{2+}) contain the aromatic thiopyrylium ion-type conjugation in the canonical formulae. Although the extremely low solubility prevents the exact measurement of oxidation potential, **5** shows one redox wave at +0.72 V vs. SCE with the peak separation by 150 mV in its cyclic voltammogram (in CH_2Cl_2 with 0.1 M n-Bu_4NClO_4, scan rate 100 mV/s, working electrode Pt, at room temperature). The potential is slightly more positive than that of **4** (0.65 V).[6)] This first electron transfer might be attributable to the formation of $5^{+\cdot}$. Selected physical properties of **4** and **5** are summarized in Table 1.

Table 1. Some physical properties of **4** and **5**

	Appearance	Mp /°C	λ_{max} /nm	E^{ox} /V vs. SCE
4	green needles	233	550	0.65, 0.81
5	dark violet needles	>300	624	0.72

We prepared CT complexes of **4** and **5** with DDQ, $TCNQF_4$, and TCNQ as acceptors, all of which possess 1:1 stoichiometries determined by elemental analyses. Their selected data are compiled in Table 2. The differences between oxidation potential of the donor and reduction potential of the acceptor, $\Delta E^{o,r}$, roughly correspond to the intermolecular HOMO-LUMO gaps for the two components and have been shown to be a convenient measure to estimate the degree of CT, Z, of 1:1 complexes.10-12) In our case, the $\Delta E^{o,r}$ values for the combination of the two donors with DDQ and $TCNQF_4$ are in positive region near zero, so-called neutral-ionic boundary,13) to predict moderate CT, and the values with TCNQ are large to predict small CT. In agreement with the prediction, Z-values determined by IR procedure14) for the complexes of **4** and **5** with TCNQ reveal their non-ionic nature. On the other hand, infrared frequencies (ω_{CN}) for the ionic complexes of $TCNQF_4$ with TTF, TMTTF, HMTTF, and TMTSF are 2202, 2207, 2201, and 2204 cm^{-1}, respectively, while that of neutral $TCNQF_4$ is 2227 cm^{-1}. These data suggest that **4**-$TCNQF_4$ (ω_{CN}=2203 cm^{-1}) and **5**-$TCNQF_4$ (ω_{CN}=2202 cm^{-1}) are also ionic complexes.15) At this stage, we could not estimate Z for the two DDQ complexes. Interestingly, however, the electrical resistivities of **4**-DDQ and **5**-DDQ complexes for the compacted powders are relatively low. These CT complexes represent the rare examples of CT complexes with relatively low resistivities despite having neither TTF-type donor nor TCNQ-type acceptor.9)

Table 2. Selected properties for the CT complexes of **4** and **5**

	4-DDQ	**4**-$TCNQF_4$	**4**-TCNQ	**5**-DDQ	**5**-$TCNQF_4$	**5**-TCNQ
$\Delta E^{o,r}$ /V	0.13	0.09	0.42	0.02	0.16	0.47
ω_{CN} /cm^{-1}		2203	2222		2202	2220
Z		ionic	0.1		ionic	0.15
ρ /Ωcm (Ea /eV)a)	38(0.1)	10^3(0.19)	10^8	420(0.12)		$6x10^6$

a) Compacted powder measurements.

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7) To a stirred mixture of $AlCl_3$ (25 g) and NaCl (10 g) was added a finely ground mixture of **4** (2.0 g, 4.8 mmol) and NaCl (10 g) at 240-250 °C during 30 min. After stirring for 30 min at this temperature, the mixture was poured over ice. The precipitates were collected by filtration and were extracted with CS_2 using a Soxhlet extractor to afford **5** (640 mg, 32%) as dark violet needles (mp >300 °C).

8) **5**: MS m/e 414 (M^+, 4%); ^1H NMR (360 MHz, $CS_2+CD_2Cl_2$) δ 6.81 (d, 2H, J=8.0), 7.06 (t, 2H, J=8.0), 7.52 (d, 2H, J=8.0), 7.4 (ABC of ABCX, 6H), 8.25 (d-like, X of ABCX, 2H, J=8.5); UV/vis (CH_2Cl_2) λ_{max} 254 (log ε, 4.79), 302 (4.61), 328 (4.30), 342 (4.39), 580 (4.34), 642 nm (4.50).

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15) Each IR spectrum was calibrated with indene as standard.

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